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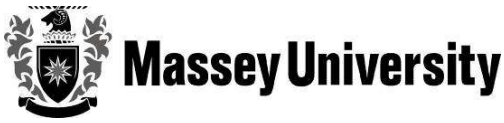
THE DEVELOPMENT AND ASSESSMENT OF ALTERNATIVE TECHNIQUES TO IMPROVE THE AGRONOMIC VALUE OF DOROWA PHOSPHATE ROCK (ZIMBABWE)

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy in Soil Science



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Abstract

Agronomically effective P fertilisers are unavailable to most smallholder farmers in Zimbabwe due to the high costs of manufacture and transportation. While phosphorus (P) deficiency remains widespread in these smallholder farming areas, farmers have limited options to ameliorate their soils leading to recurring food insecurity problems. The aim of this thesis was to develop alternative P sources with good agronomic value using locally available materials and alternative techniques such as thermal alteration, co-pyrolysis, and acid leaching.

In-order to design alternative techniques, chemical and physical characterisation of the local Dorowa phosphate rock (DPR) was conducted. The DPR contained 89% and 3.5% apatite (hydroxy-fluorapatite) and calcite ($CaCO_3$) respectively and had a total P (TP) content of 16.5%. With less than 13.5% of TP soluble in 2% citric acid, DPR has limited agronomic value as a direct application phosphate rock. The cadmium (Cd) and fluoride (F) content in DPR was low at 0.16 mg kg^{-1} and 2% respectively, indicating reduced F and Cd soil contamination issues in final fertiliser products. The DPR generally contained about half the amount of Fe, Al, Mg and K that is reported in literature and this was because the current sample contained less gangue materials. When compared to previous reports on DPR, the observed differences in the current sample were likely as a result of improvements in the mining and beneficiation process, or the current grade of the ore had a higher apatite content.

To improve the agronomic value of DPR, the effect of thermal alteration of DPR in the presence of silicate materials (dunite, serpentine and recycled glass) was investigated. Sintering (heating at sub fusion temperatures) was chosen as a less energy intensive process compared to fusion. The sintered DPR mixtures (50% initial DPR content) had an increase of citric soluble P of up to 45, 53, and 73% when mixed with dunite, serpentine and recycled glass, respectively, compared to the unamended DPR. Increases in citric soluble P suggested isomorphous substitution of PO_4^{3-} in fluoro-hydroxyapatite by SiO_4^{4-} and or Mg^{2+}/Na^{+} for Ca^{2+} and Fe^{2+}. The sintered products that had high citric soluble P indicated that they might have improved agronomic value and were recommended for further testing in a glasshouse.

Another technique where the DPR was added to maize stover residues (stems + leaves) and pyrolysed at 450 ^{o}C was developed and assessed for potential to improve the

agronomic value of DPR. A suite of biochar-based fertilisers (BBFs) were obtained from pyrolysis of DPR + maize residues mixed at w/w ratios of 1:2, 1:4, 1:6, and 1:8 (DPR/ maize residues). Except for the 1:2 mixture, co-pyrolysis DPR with maize stover resulted in increases in biochar yield, carbon retention and nitrogen retention of at least 26, 43, and 26% respectively, compared to the pyrolysis of maize stover alone. The 1:6 and 1:8 mixtures produced biochar with more than a 30% increase in citric soluble P compared to the unamended DPR. The results showed that there was potential for on-farm co-pyrolysis of crop wastes with DPR to produce a P source with greater agronomic value. From these results, the 1:6 mixture that had 5.6% total P and 33.6% of the total P citric soluble, was recommended for testing in the glasshouse.

The potential of using pyrolysis condensate as a cheaper acid source to recover P from DPR using sequential extractions was also evaluated. Before pyrolysis condensate could be used there was need to ascertain how much P could be recovered from DPR by the common organic acids; citric, acetic, and oxalic acids at various pH values, and then sequentially leached. Results showed that a suspension pH of 3 was necessary for maximum P recovery with citric and oxalic acids solubilising about 21.9 and 46.3% of the total P in DPR respectively, after 3 extractions. The greater P recovery under oxalic acid was attributed to the acid's ability to remove Ca from solution as evidenced by the Ca:P molar ratio in oxalic acid leachates, which was at least 3 times less than that of other acids tested. Given this potential, a mixture of organic acids in pyrolysis condensate produced from maize stover were evaluated for their P recovery ability. Despite the high acidity and a pH of 3 maintained in leachates, sequential leaching extractions with the aqueous phase pyrolysis liquid over 26 hours was relatively ineffective, solubilising less than 14% of the total P in DPR.

Four of the alternative P sources that were developed exhibited high potential agronomic value and were further evaluated for agronomic effectiveness in the glasshouse using broccoli and ryegrass as test crops. After 6 harvests, ryegrass that had been fertilised with DPR: biochar (1:6) or sintered DPR + recycled glass (50%), had similar P uptake and produced at least 95% of the biomass produced when monocalcium phosphate (MCP) was applied at the same citric soluble P rate. The same alternative P sources produced broccoli biomass yields and P uptake that was either comparable to or higher than when MCP was applied. The DPR co-pyrolysis biochar and recycled glass (50%) sintered P sources would provide a good option for smallholder farmers around the Dorowa area in Zimbabwe where PR is mined. However, larger scale field studies are recommended.

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Acronyms

AES	Atomic Emission Spectrophometer
BBF	Biochar Based Fertiliser
BPL	Bone Phosphate of Lime
C	carbon
CCE	Calcium Carbonate Equivalent
Citsol	Citric soluble
Cum. As Rec	Cumulative as received
Cum. Ground	Cumulative ground
DI	Deionised Water
DPR	Dorowa Phosphate Rock
DSC	Differential Scanning Calorimetry
Dun	Dunite
FTIR	Fourier Transform Infrared spectrophotometry
GHG	Green House Gas
HMF	Hydroxyl-methyl-furfural
hr	hour
ICDD	International Centre for Diffraction Data
IFDC	International Fertiliser Development Centre
LMWOA	Low Molecular Weight Organic Acid
LSD	Least Significant Differences
MANOVA	Multivariate Analysis of Variance
MPAES	Microwave Plasma Atomic Emission Spectrophotometry
NAC	Neutral Ammonium Citrate
ORE	Ore Research and Exploration
P	Phosphorus
PR	Phosphate Rock
REE	Rare Earth Element
SEM	Standard Error of Means
Serp	Serpentine
SSP	Single Super Phosphate
TAN	Total titratable Acid Number
TGA	Thermo-gravimetric Analysis

UV-VIS	Ultraviolet visible region
WAP	Wet Acid Process
XRF	X-ray Fluorescence

CHAPTER 1

GENERAL INTRODUCTION

1.1 General background

The result of the unavailability of agronomically effective nutrient sources plays out against a backdrop of low fertility soils causing recurring food insecurity problems in many African smallholder farming systems. Soil nutrient limitations, especially phosphorus (P) deficiency are widespread in African farming areas and limit crop responses to other non-deficient nutrients (Bonzi *et al.*, 2011; Giller *et al.*, 2011; Mafongoya *et al.*, 2006). Soil P deficiencies result from low total P content as a result of the type of soil-forming parent material and or P fixation by aluminium and iron oxides in highly weathered tropical soils (Chikowo *et al.*, 2009; Nyamangara *et al.*, 2020), see also Chapter 2.1. While farmers understand the need to apply external nutrient sources for improving crop production, they apply below optimum levels due to the lack of access and affordability of inorganic fertilisers (Mtali-Chafadza *et al.*, 2020; Kihara *et al.*, 2016; Mafongoya *et al.*, 2006). In some African countries such as Zimbabwe and Malawi, the government has tried to encourage smallholder farmers to use more fertilisers by offering subsidies and or small fertiliser starter packages. However, as Ricker-Gilbert and Jayne (2017) report, the effects of subsidy programmes can be severely limited and non-enduring. As a result, the same authors recommended that addressing soil fertility issues make more sense in improving profitability and sustainability.

The major factors driving the cost of inorganic P fertiliser in Zimbabwe are the high acidulation costs that employ the use of imported sulphur, and excessive transportation costs as a result of deteriorating road infrastructure (Tumbure *et al.*, 2019). The volatile Zimbabwean economy is bedevilled with foreign currency shortages and liquidity challenges (Pasara and Garidzirai, 2020) that further complicate the P fertiliser manufacturing industry (Tumbure *et al.*, 2019). The use of low-cost alternatives made

from local phosphate rock (PR) for crop production could provide sustainable relief for smallholder farmers. However, the pursuit to realise the potential of alternative P sources such as direct application of PRs is faced with numerous hurdles. First amongst these challenges is the un-reactive nature of local igneous PRs which limit their agronomic value (see Chapter 2.3). There are no adopted and reported commercial success stories involving the use of directly applied igneous PRs despite numerous research on the same (Nandwa and Bekunda, 1998). Furthermore, the lack of agronomic effectiveness of directly applied PRs available in Zimbabwe has been reported on numerous occasions (Govere *et al.*, 2003; Nezomba *et al.*, 2007; Govere *et al.*, 2005; Soropa *et al.*, 2012). Smallholder farmers have therefore lost interest in using igneous PRs for short term crop production benefits (Vanlauwe and Giller, 2006).

Dorowa PR (DPR) is the only commercially extracted phosphate ore in Zimbabwe and it is a low grade ore that has a head grade of between 2.6 to 3.5% P with a P_20_5:CO_2 ratio of 6:1 (Barber, 1991). While naturally high-grade ores (P > 11%) are preferred for fertiliser production to reduce cost (Aydin *et al.*, 2009), these are not available in Zimbabwe. The phosphate in the rock has to be first concentrated by grinding, wet magnetic separation (to remove magnetite), followed by de-sliming and froth flotation before acidulation can take place (Barber, 1991). Meck *et al.* (2010) explains that the grinding of phosphate rock at the Dorowa mine produces slimes that are less than 45 µm and tailings in the range 45–300 µm. Even after being processed into a concentrate, it is still un-reactive and needs to be acidulated with concentrated acid.

Local farming communities in Buhera, described as one of the poorest districts of Zimbabwe, have not been able to take advantage of the DPR that is produced in their area.

At the same time, researchers have noted that some soils in this region are P deficient (Mtali-Chafadza *et al.*, 2020; Soropa *et al.*, 2012). Research presented in this thesis was therefore guided by the need to develop low-cost alternative technologies to enable local smallholder communities to effectively use the DPR for crop production (Chapter 2.4). This would make meaningful and sustained contributions towards food production because smallholder agriculture is the major contributor to national food security in Zimbabwe (Makuvaro *et al.*, 2017).

1.2 Research objectives

The hypothesis of this thesis was that three technologies (thermal alteration, co-pyrolysis and mixed acid leaching) could be used to improve the agronomic effectiveness of DPR. The specific objectives supporting the hypothesis were;

- To characterise a more recent sample of the DPR, its P extractability and quantify the level of contaminating elements such as fluorine and cadmium.
- To investigate the effect of thermal alteration on P extractability of the DPR through sintering with a range of relatively inexpensive silicate sources.
- To assess the effect of co-pyrolysis of maize stover with DPR on P solubility, liming value and recovery of carbon (C) from biomass and DPR.
- To evaluate the effectiveness of mixed organic acids in pyrolysis condensate, derived from the pyrolysis of maize stover, in solubilising agronomic P from DPR.
- To evaluate biochar-based, glass-sintered and serpentine sintered P sources involving DPR, on growth and P uptake of annual ryegrass (*Lolium multiflorum* Lam.) and broccoli (*Brassica oleracea* var. italica).

1.3 Thesis outline

The presentation of results in this thesis follows a planned natural successional pattern of review of concepts, hypothesis testing through robust research objectives, discovery, review of results and concepts, and setting new research directions to achieve time-limited goals. This thesis has a total of 8 chapters, the first two chapters constitute a general introduction and literature review. Chapters 3-7 constitute research chapters prepared for submission/submitted or accepted as journal articles. As a result, there are some slight differences in structure as results chapters were prepared according to the different formatting requirements of different journals.

Chapter 1 provides an introduction and background to the thesis, from which the hypothesis and supporting objectives are derived.

Chapter 2 presents a current literature review of, (i) reactive and non-reactive P rocks and how they dissolve in the soil environment, (ii) techniques used for the assessment of fertiliser quality and (iii) methods of improving phosphate rock agronomic efficiency and their limitations

Chapter 3 gives an updated characterisation of the DPR that is currently being produced in Zimbabwe, its P solubility indices and issues associated with the use of DPR for fertiliser production. Chapters 4, 5, and 6 explore three alternative techniques that have the potential to create soluble P from the insoluble P minerals in DPR. The selection of the techniques is based on their practicability of operation with local resources in impoverished farming communities.

Chapter 4 explores thermal alteration of DPR mixed with various silicate sources at sub-fusion temperatures. Recycled glass, a low-cost silicate source is compared against serpentine minerals in terms of its effect on P solubility.

Chapter 5 studies the effect of co-pyrolysing DPR with maize stover on P solubility, liming value, and carbon retention of the final biochar-based product.

Chapter 6 investigates the amount of P and selected minerals that can be solubilised from DPR by various organic acids and evaluates the potential of mixed organic acids in pyrolysis condensate in solubilising DPR. The products manufactured in Chapters 4- 5 that had citric soluble P contents that exceeded 30% were trialed for their agronomic effectiveness in a glasshouse trial

Chapter 7 investigates the agronomic effectiveness of fertiliser products produced in Chapter 4 and Chapter 5, in ryegrass and broccoli glasshouse trials.

Chapter 8 presents an overall summary of the thesis and discusses recommendations for further development and application of research ideas presented in the thesis.

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CHAPTER 2

LITERATURE REVIEW

The research objectives of this thesis (in Chapter 1) require a thorough understanding of:

(i) the nature of P deficiency in tropical soils

(ii) the advantages/disadvantages and limitations of the use of local PRs to relieve P deficiency

(iii) the analytical and experimental procedures for estimating PR agronomic potential

(iv) current alternative methods to improve agronomic efficiency of PRs and their limitations

This chapter reviews literature in the above topics. Some generic literature will also be reviewed in this chapter and other more specific material will be covered in the introduction to each experimental chapter.

2.1 Reactive and nonreactive phosphate rocks in the soil environment

2.1.1 Introduction to tropical soils and their P management needs

The clay fraction of highly weathered tropical soils contains Fe and Al oxides that form the predominant minerals goethite, hematite and gibbsite which are effective at attracting anions due to their variable pH-dependent surface charge (Juo and Franzluebbers, 2003). In an acidic environment, secondary forms of phosphate minerals are formed as phosphate anions in soil solution form strong chemical bonds with Al and Fe oxide minerals. The irreversible binding of phosphate anions to Fe and Al oxides in acidic conditions makes soil P unavailable for plant uptake and is termed P fixation. Given that about 43% of the land area in the tropics is occupied by acidic soils (Abd El-Halim and Omae, 2019), soil P deficiencies are commonly exhibited (Mwangi *et al.*, 2020; do Carmo *et al.*, 2019; Barreto *et al.*, 2018; Calle-Castañeda *et al.*, 2018; Rafael *et al.*, 2018). In addition to P deficiencies, P-fixation in soils often results in a low plant uptake efficiency of commercial water-soluble P fertilisers (Chien, 2019) which can be as high as 80% of the P fertiliser applied (Ahmad *et al.*, 2019).

The use of slow release phosphate rocks (PR) has been suggested to better manage P supply to growing crops. However, in sub-Saharan Africa where PR deposits are abundant, they have not been fully utilised because of their low solubility (un-reactiveness) and/or content of gangue minerals (Nakamura *et al.*, 2020). The solubility characteristics of PRs are described in the next section.

2.1.2 Intrinsic PR factors affecting their solubility (bioavailability)

Phosphate rocks can be mainly classified into phosphorites (of sedimentary origin) and carbonatites (of igneous origin), and have widely differing mineralogical, textural and

chemical characteristics (Van Kauwenbergh, 2010; Silva *et al.*, 2019; Rafael *et al.*, 2018; Bustamante *et al.*, 2016). The most abundant phosphate deposits in southern Africa are igneous (Van Kauwenbergh, 1991). The bio-availability of P present in PRs is strongly dependent on the rock's chemical, physical, and mineralogical/crystallographic properties which affects its agronomic potential (IFA, 2013; Aydin *et al.*, 2009).

The main component of PR is calcium apatite which can exist with numerous elemental substitutions, and varied crystal perfections (degree of point, line, or planar defects in the crystal lattice) (Tõnsuaadu *et al.*, 2011). Sedimentary PRs usually contain carbonate-fluorapatite varieties (francolite) while igneous PRs usually contain fluorapatite, hydroxyapatite, or chlorapatite (Van Kauwenbergh, 2010). A greater degree of carbonate substitution (more francolite) in sedimentary PRs provides greater reactivity (Charanworapan *et al.*, 2014) and higher solubility in acidic soils. The crystal lattice parameters, structure, and crystallinity of apatite crystals vary with chemical substitutions (Tõnsuaadu *et al.*, 2011). Igneous PRs, such as Dorowa PR (DPR) from Zimbabwe, are usually coarsely crystalline (Govere *et al.*, 2003). Particle size distribution also affects the reactivity of PRs, and grinding to a smaller particle size causes crystal structural defects, that result in the incorporation of CO_2 and formation of OH^- in the apatite structure leading to greater PR reactivity (Fang *et al.*, 2019). To gain an insight into the mineralogy of PR, X-ray diffraction (PXRD) techniques are employed.

Generally, PRs are termed 'reactive' when at least 30% of the P is solubilised by 2% citric acid (Braithwaite *et al.*, 1990). Finely divided reactive PRs (95% of particles <63 μm) are suitable for direct application to acidic soils (Bolan *et al.*, 1993). Reactive PRs are

generally derived from sedimentary deposits, whereas igneous PRs are mostly unreactive (Bolan *et al.*, 1993).

The characterisation of the DPR by X-ray diffraction and X-ray fluorescence will be undertaken in Chapter 3 where the emphasis will be on the DPR's physical properties and chemical constituents that could be of concern when working with this PR for fertiliser production.

2.1.3 Soil and climate conditions controlling agronomic effectiveness of PRs

In addition to PR intrinsic factors, the soil conditions and environment (climate) also influence the overall ability of PRs to supply available P to growing crops. The reported effectiveness of PRs directly applied to soils shows substantial variation, due to PR reactivity, soil conditions, and crops grown (Nakamura *et al.*, 2020). Soil conditions, such as soil water regimes, pH, organic matter content, microbial activities, and P retention, can limit P supply to crops from applied PRs (Nakamura *et al.*, 2019; Ahmad *et al.*, 2019; Bustamante *et al.*, 2016). Phosphate rocks are fundamentally water insoluble and need acidic conditions for dissolution to occur, so that soil pH has a strong effect on PR dissolution (Bolan and Hedley, 1989). The mechanisms by which PRs dissolve in soil solution requires water-filled pore space that will allow organic acids, and other chelating, and complexing agents produced by plants and microorganisms to diffuse to and react with the PR surface (Wang *et al.*, 2020a; do Carmo *et al.*, 2019).

Organic acids that are secreted from plant roots and soil microorganisms such as fungi, lichens, and prokaryotes help to solubilise P in the rhizosphere (Rafael *et al.*, 2018). Microbial secretions that include acids and other chelating substances are primarily

released during organic matter decomposition in the soil (Bustamante *et al.*, 2016). The microbially mediated oxidation of N, C, and S in soil is another source of acidity that promotes dissolution of PRs. Sulphur can be biologically oxidised and converted to sulfuric acid by microbes especially those of the genus *Thiobacillus* (Aria *et al.*, 2010; Jazaeri *et al.*, 2016; Loganathan *et al.*, 1994). However, populations of *Thiobacillus* in soils are often very low being limited by low soil pH, low organic matter content, high temperatures and prolonged periods of dryness (Jazaeri *et al.*, 2016). Limited water-filled pore space in the soil profile will reduce PR dissolution in soil. In addition, the plant rhizosphere may not be acid if an excess of anions is taken up by plants over cations (Evans and Price, 2008). This typically occurs when the form of nitrogen supply is nitrate, rather than ammonium or organic N.

As a result of the many factors controlling PR dissolution discussed above, optimal conditions needed for PR dissolution are usually not met. This gives rise to the need to optimise PR dissolution in soils by altering the PR, and/or altering the soil conditions. Before any potential strategy can be tested, there is a requirement to define the 'quality' of the PR which is achieved through several methods accepted by researchers in this field. Aspects of PR quality, and the analysis for such, are discussed in the next section (2.2). Strategies to achieve improved PR agronomic efficiency are further discussed in section 2.3 of this chapter.

2.2 Fertiliser quality analysis of PRs

2.2.1. Total elemental content, impurities and mineral phases

Knowledge of total elemental content and their speciation in PRs is crucial for identifying possible environmental contamination issues associated with the use of PR in agricultural

soils. Because of the possibility of contamination through the use of PRs and their products, various governments have set standards for allowable limits of unwanted contaminants in PRs and fertilisers. Environmental contaminants from PR and PR products can be grouped into radioactive elements, trace metals, and rare earth elements (REEs) (Wang *et al.*, 2020b). Toxic trace elements such as cadmium are usually higher in sedimentary PRs than igneous PRs (Wang *et al.*, 2020b), while PR products from igneous carbonatites are more enriched in REEs than in sedimentary PR products (Silva *et al.*, 2019). The accumulation of Cd in agricultural soils as a result of phosphate fertilisation may lead to its uptake and accumulation in consumed foods that may cause kidney diseases (Roberts, 2014). The potential of Cd uptake is increased due to its persistence in soils after continuous fertilisation with high Cd containing fertilisers.

High levels of fluoride (F) in fertilisers increase the risk of chronic F toxicity or acute F poisoning when livestock directly ingest soil while grazing in recently fertilised pastures (Cronin *et al.*, 2000). High F concentrations in soil could also negatively affect the biomass and respiration of soil microbes (Wang *et al.*, 2019; Mendes *et al.*, 2013). It is therefore prudent to undertake an analysis of the F and Cd content of PRs intended for use as fertilisers to safeguard against potential environmental contamination and toxicity issues.

Several techniques for the analysis of total elemental content in PRs have been developed which include spectrophotometry after acid digestion, and X-ray fluorescence (XRF) techniques. The accuracy of techniques involving wet digestion is dependent on complete dissolution during the digestion stage, and the potential of ionic interference using spectrophotometry. In this thesis, wet digestion, microwave plasma atomic emission

spectrophotometry (MPAES), atomic absorption spectrophotometry (AAS), and XRF techniques were used (Cevik *et al.*, 2010; Kruse *et al.*, 2015). For fluorine analysis, potentiometric ion selective electrode (ISE) was used (Grace *et al.*, 2010). This method is widely used compared to titrimetric and spectrophotometric methods for the analysis of F in phosphate rocks because of its simplicity and minimal labour requirements. Sredovic and Rajakovic (2010) describe the ISE method as convenient with a relative standard deviation of <5%, and an F recovery of more than 95%. However, certain considerations should be taken to avoid errors in measurement. These include maintaining the hydroxyl concentration below 10% since the ISE responds to hydroxyl ions and removal of interference caused by Si^{4+}, $Al^{3+,}$ and Fe^{2+} (Al-Othman and Sweileh, 2000). Before analysis by an ISE, precipitates of $Al^{3+,}$ and Fe^{2+} are removed by filtering after adjusting the pH of the analyte to 8.5 (Loganathan *et al.*, 2001).

2.2.2 Analysis of PR reactivity through lab scale extractions

To gain an insight into the value of phosphate rock deposits for agronomic use, various laboratory analytical techniques are employed which include both chemical and structural methods. Laboratory methods have the advantage of being quick and easy to conduct compared to field methods. However, limitations exist as discussed in this section.

Chemical reactivity or solubility has been extensively used as an indicator of a PR's suitability for phosphate fertiliser production, and/or for direct application to the soil (Abouzeid and El-Jallad, 1980; Mackay *et al.*, 1984; Chien and Menon, 1995). While extraction in 2% citric acid, 2% formic acid, and neutral ammonium citrate is prominent (Chien, 1993), other studies reported inconsistent results, alluding to the depressive effect of calcium, phosphate, carbonate, iron and aluminium ions (Braithwaite *et al.*, 1992).

The presence of water-soluble ions, such as calcium and phosphate, may exert a common-ion depressive effect on apatite solubility, and free carbonates may raise pH if a single extraction is performed (Chien *et al.*, 2011). As a result, a second sequential extraction procedure for neutral ammonium citrate has been adopted by some international laboratories to eliminate the effects of free carbonates in the first extraction step (IFA, 2013). However, ranking systems based on single extractions, such as the one proposed in the earlier work of (Diamond, 1979), are still used widely today (Table 2.1).

Table 2.1 Phosphate rock ranking system according to solubility in common extractants for assessing direct application potential

Agronomic potential	**Soluble P (% w/w)**		
	Neutral ammonium citrate	**2 % Citric acid**	**2% Formic acid**
High	> 2.35	> 4.1	> 5.67
Medium	1.4 - 1.96	2.92 - 3.66	3.05 - 4.71
Low	< 1.18	< 2.62	< 2.53

Source; (Van Kauwenbergh, 2006)

Although solubility has been used to screen PR materials, the actual relative agronomic effectiveness (RAE) of PR in the field varies widely because there are complex interactions between the fertiliser material, soil, crop, and land management (Chien and Menon, 1995). Assessment of a PR's reactivity through chemical extraction does not consider environmental factors such as rainfall, biological activity, soil type, and soil nutrient status, that also determine agronomic effectiveness. Although useful, common standard solubility tests are only qualitative in nature because of their limited focus on predicting a short-term agronomic value (Gholizadeh *et al.*, 2009).

The chemical analysis and reactivity classification of the DPR will be undertaken in Chapter 3 where the focus will be on its suitability for agronomic use when unmodified, or as a raw material for fertiliser production.

2.3 Agronomic potential of the DPR - inferences from literature

The DPR that is mined in Buhera district, Zimbabwe is an igneous hydroxy-fluorapatite (Ca_5 $(PO_4)_3$(OH, F, Cl) with at least 50% apatite content (Govere *et al.*, 2003; Meck *et al.*, 2011). The ore has a head grade of between 2.6 to 3.5 % P with a P_20_5:CO_2 ratio of 6:1 (Barber, 1991). A concentrate of the rock phosphate is made by grinding the rock and then removing magnetite by wet magnetic separation, followed by de-sliming and froth flotation (Barber, 1991). Grinding of the DPR at the mine produces slimes that are less than 45 µm, with tailings in the range 45–300 µm (Meck *et al.*, 2010). The available characterisation data of the DPR is about 30 years old and describes the final rock concentrate as containing approximately 14.52 % P, 78 % apatite, and 1.6 % fluorine (Van Kauwenbergh, 1991).

While different researchers have reported different citric acid and neutral ammonium citrate solubility values for DPR, all reported values occupy the low solubility range (Table 2.1). For example, Smalberger *et al.* (2006) reported the solubility of DPR in 2 % citric acid to be 0.78% P. Another study by Govere *et al.* (2003) reported a citric solubility of 1.05 % P, while IFA (2013) reports it to be 1.83 % P. Smalberger *et al.* (2006) reported the NAC solubility of the DPR to be 0.52 % P, and IFA (2013) 0.65 % P. Varying values for solubility could be due to differences in sampling procedures and/or mining batches.

The few available studies on DPR show that it is ineffective as an immediate P source when directly applied to acidic soils. For example, Govere *et al.* (2005a) and Govere *et al.* (2003) reported the direct application of DPR at 150 mg P/kg soil (soil pH 4.8) to be ineffective in improving P uptake of maize and ryegrass, respectively. Nezomba *et al.* (2007) also reported no significant improvement in the total biomass of legume and grass species after application of DPR at 26 kg P ha $^{-1}$, in Zimbabwe.

2.4 Alternative methods of improving the agronomic efficiency of PRs

At least 91% of global phosphate concentrates are processed into fertilisers using inorganic acids (Hermann *et al.*, 2014). When sulphuric acid is used to process PR, the general equation can be written as (2.1):

$$Ca_{10}F_2(PO_4)_6 + 6H_2SO_4 + 15H_2O \rightarrow 3Ca(H_2PO_4)_2.H_2O + 6CaSO_4.2H_2O + CaF_2 \qquad (\mathbf{2.1})$$

At present, acid processes are more economic for fertiliser production since the sulphur needed for sulfuric acid (H_2SO_4) production is usually obtained as a by-product from petroleum refineries and/or natural gas beneficiation (Haneklaus *et al.*, 2015). However, this source of S is not locally available for southern African countries which must import it. The low foreign currency reserves in Zimbabwe (Herald, 2020; Jefferis, 2020) mean that this source of S is more expensive to import, and this drives up the price of the phosphate fertiliser produced. Alternative methods are therefore required that can take advantage of locally available resources and/or reduce costs.

2.4.1 Thermal treatment of PRs

The crystalline structure of PR minerals can be altered using thermal energy (with or without addition agents), with the objective of making the P in the apatite structure citrate soluble. When PR alone is heated (called calcination), a product may result with a collapsed crystal structure that leads to greater P solubility in citric acid or neutral ammonium acetate (Francisco *et al.*, 2007). The calcination process results in a loss of hydration water, F, and the breaking down of carbonates, resulting in structural disorganisation (Francisco *et al.*, 2007; Watti *et al.*, 2016). Calcination is usually undertaken to enrich raw PR. Fertilisers are produced when the PR is heated with other substances such as carbonates, silicates, and alkaline earth chlorides (called sintering and smelting) (Watti *et al.*, 2016).

Sintering occurs when the added thermal energy does not result in melting the PR mixture, while smelting/fusion occurs when the PR mixture melts. Rhenania phosphate is produced from sintering the apatite phosphate with sodium carbonate and silica in the presence of water vapor at a temperature range between 1100 - 1200 ^{o}C (Watti *et al.*, 2016). Rautaray *et al.* (1995) found that Indian phosphate rocks mixed with Na_2CO_3 in the ratio 2:1 (PR/ carbonate) and heated for 2 hours at 900 °C resulted in superior agronomic effectiveness.

When mixed with silicates, heating PRs that contain S can result in isomorphous substitution of $2PO_4^{-3}$ by both SiO_4^{-4} and SO_4^{-2} where the substituents enter the apatite structure through the vacant orthophosphate positions where carbonates have been driven off (Knubovets *et al.*, 1997). Soluble phosphate compounds, known as fused magnesium phosphate (FMP) with alkaline characteristics suitable for acidic soils, are produced (da

Silva and Kulay, 2005). Early studies by Walthall and Bridger (1943) in pot culture studies, found comparable effectiveness to superphosphate when a product of high-grade Tennessee PR and olivine in the ratio 1:0.46 respectively, and fused at 1550 ºC, was used. The fused product had 22.8% total P_2O_5 and 21.4% soluble P_2O_5 with about one third of the fluorine volatilised. Boylan (1952) highlights that the $Si0_2/P_20_4$ molar ratio should be 2.0 or greater to obtain products with a high P availability. Fused Ca-Mg phosphate fertilisers with citric acid solubilities between 20% P_2O_5 to over 90% are currently produced in Japan, Korea, Taiwan, China, Brazil, and South Africa (Hermann *et al.*, 2014).

It should be noted that igneous PRs usually have significantly different mineralogy than sedimentary PRs, and include associated gangue minerals (Kawatra and Carlson, 2014). As a result of this, differences are expected when it comes to optimising fusion mixture ratios and fusion temperatures. There is potential to use local magnesium silicate resources in sintering/fusion mixtures with DPR. An economic evaluation of such a method would be required after ascertaining ideal mixing ratios and fusion/sintering temperatures for greater P solubility. The proximity of magnesium silicate minerals such as the Shawa vermiculite deposit (<100 km) would also be advantageous. For example, The Shawa vermiculite deposit is located near the DPR mine, with the deposit being described as one of the largest vermiculite deposits in the world. The vermiculite is hosted within ijolite and serpentine rocks and is largely composed of serpentinised dunite (Harmer *et al.*, 1998). The vermiculite is about 36 - 39% SiO_2 and 24 -26% MgO on a weight basis.

The major drawback of the thermal processes described above is the relatively large amounts of energy required which becomes very costly (Haneklaus *et al.*, 2015). As a result, Rhenania phosphate has since disappeared from the European market, with the last Rhenania phosphate plant in Germany shutting down in 1982 (Hermann *et al.*, 2014). The other disadvantage of Rhenania type phosphates is the expense of addition agents such as sodium carbonate (Walthall and Bridger, 1943). Solar powered furnaces can be explored with the intention of bringing the cost down as well as sintering at sub-fusion temperatures (Baeyens *et al.*, 2019).

In Chapter 4 of this thesis, glass and New Zealand serpentine and dunite are used in thermal experiments with DPR to test whether low temperature sintering/fusion will significantly improve P solubility.

2.4.2 Techniques to achieve in-situ dissolution of PRs

Low cost acidulation of PR using composting/fermentation techniques have been favoured as technologies that suit rural communities. Composting and fermentation of wastes mixed with PR can encourage P dissolution from PR through release of the organic acids generated by microbial activity that chelate Ca^{2+} and other cations, with a short initial period of high acidity (Walker *et al.*, 2012). Other mechanisms, by which organic amendments improve dissolution of PR are the release of protons from microorganisms (Golabi *et al.*, 2007). Addition of organic matter also increases phosphate-solubilising microorganisms (PSM) (Wickramatilake *et al.*, 2011). Phosphate from the organic matter can be co-released by hydrolytic enzymes, including phosphatase enzymes which breakdown ester bonds between the phosphate group and the organic residue.

A distinct disadvantage of in-situ systems is that microbes are exposed to various chemical elements released from the PR, especially F that causes most of the microbial PR solubilisation systems to operate at suboptimal conditions (Mendes *et al.*, 2013). For example, in Fan *et al.* (2012)'s incubation study with PR and *Thiobacillus* spp, the net production of plant-available P from PR was substantially reduced because of a build-up of active Fe and Al ions in solution at the low soil pH. Another challenge is that a greater part of P dissolution and fermentation research has focused exclusively on simple, chemically pure, sugars and inexpensive carbohydrate sources, are largely ignored as fermentation media (Vassilev *et al.*, 2014). Nevertheless, the biological extraction of P from PR is described as less expensive, less energy intensive, and more environmentally friendly, compared with the acidulation conventional process (Gaind, 2016).

Co-granulation of unreactive PRs with soluble P and other essential elements has also received research attention. Contrasting results, however, have been reported for DPR. In a study by Soropa *et al.* (2012) there was no significant effect on maize biomass and P uptake in greenhouse studies when DPR was pelletised with SSP and added to cattle manure. Govere *et al.* (2005b) reported that when the DPR was pelletised with SSP (P ratio 50:50), urea, and KCl, it was as effective as SSP. However, SSP, urea and KCl, will have increased the production cost of this process, a reason that could have led to the non-adoption of this method.

2.4.3 Pyrolysis condensate as an alternative acid source for ex-situ dissolution of PRs

Rather than composting or including PR in microbial cultures, ex-situ dissolution has the advantage of being able to encourage optimal acid and enzyme production without toxicity-related limitations resulting from the dissolution of other elements from the PR.

Greater acid titres can be obtained first through processes such as fermentation or pyrolysis, and then used to solubilise the PR.

With increasing interest in producing biochar as a GHG mitigation technique (Carneiro *et al.*, 2018; Domingues *et al.*, 2017), interest in pyrolytic processes is also increasing. While the main product of pyrolysis, biochar, has found many uses as a soil amendment, other by-products, particularly the condensate liquid fraction, are challenging to utilise because of the wide variety of compounds in these by-products (Keskinen *et al.*, 2017). The water-soluble organic products found in the condensate liquid fraction include sugars, acids, furans, furfurals, etc (Hoekman *et al.*, 2013). The amount and type of by-products depend on the feedstocks used, and the reaction conditions employed such as pyrolysis temperature, and time to reach maximum temperature. So far, pyrolysis processes have primarily focussed on the production of biochar or hydrochar, with little consideration of the by-products (Licursi *et al.*, 2017). Research to establish practical techniques to isolate individual components from the condensate liquid fraction is still in its infancy. Keskinen *et al.* (2017) explains that unambiguous methods have not been recognised yet, and a greater need exists for new ways to utilise pyrolysis by-products.

There is a potential to utilise the acids in the condensate liquid fraction to solubilise low grade PRs such as the DPR. If effective, this may prove to be an economical method for producing phosphate fertiliser since agro-wastes can be used in the pyrolysis process. Pyrolysis has a promising potential to treat underutilised lignocellulosic biomass into biochar and organic acids (Kambo *et al.*, 2017).

Reports from literature show a wide variation in the amount of organic acids in the condensate liquid fraction because of the wide variety of biomass feedstock used, and the range of reactor conditions. There is also a lack of uniformity when reporting the acids produced, with some studies stating concentrations, and others stating quantities per unit dry biomass used. Licursi *et al.* (2017) reported quantities of acetic acid, levulinic acid, and formic acid (expressed as % of the dried biomass) of 11.6, 9.2 and 4.5% respectively, when milled hazelnut shells were pyrolysed at 180 ^{o}C for 90 minutes. In the same study, when the reaction time was increased to 180 minutes, the quantities of acetic acid, levulinic acid, and formic acid were 6.9, 12.5 and 7.6% respectively. In Keskinen *et al.* (2017)'s study, pyrolysis in water (called hydrothermal carbonisation (HTC)) was compared with slow pyrolysis using willow (salix) as the feedstock. The major organic acid produced was acetic acid at 12 and 150 g L^{-1} for HTC and slow pyrolysis respectively. The temperature and residence times were 260 °C and 6 hrs for HTC and 375-475 °C and 3hrs for the slow pyrolysis. In another study by Kambo *et al.* (2017) in which miscanthus was used for HTC, pyrolysis condensate liquid with increased acidity was produced when the temperature was increased from 190 to 260 °C, with process water re-circulated 10 times at a residence time of 5 mins. The major acids produced at 260 °C were acetic acid at 27.5 g L^{-1}, levulinic acid at 15 g L^{-1}, glycolic acid at 19 g L^{-1} and formic acid at 6 g L^{-1}.

The major acid produced in pyrolytic processes is usually acetic acid. While purification of acids in pyrolysis condensate would be needed for other processes, there is no need to purify these acids for PR solubilisation. The only requirement would be to separate the tar and aqueous components. The potential to solubilise the DPR, using acid mixtures in the condensate liquid produced from the pyrolysis of agro-wastes, requires investigation.

If effective, this may be an economic pathway for soil fertility amelioration. In chapter 5 and 6 of this thesis, the potential for producing biochar with higher agronomic value from co-pyrolysis of DPR and biomass, and the potential of using pyrolysis condensate to solubilise P from DPR, is evaluated.

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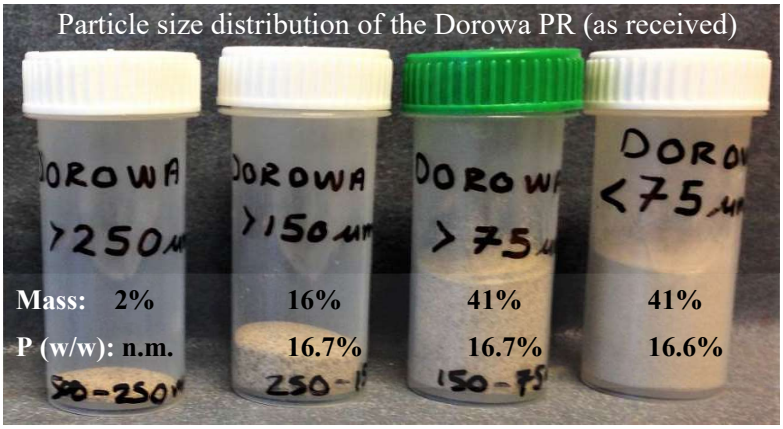
CHAPTER 3

UPDATED CHARACTERISATION OF DOROWA PHOSPHATE ROCK MINED IN ZIMBABWE

As discussed in Chapter 2, the knowledge of elemental content in phosphate rocks (PR) is essential for predicting potential environmental contamination issues and to comply with governmental and trade regulations. In this chapter, a discussion of the chemical and physical nature of the Dorowa PR is presented. The agronomic potential of the Dorowa PR as a direct application is also discussed, setting a foundation for succeeding experimental chapters.



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Abstract

The physical and chemical characteristics of mined phosphate rock concentrate will vary temporally as the location and nature of the ore body changes and the type of equipment used in the beneficiation processes change over time. For Dorowa phosphate rock (DPR) in Zimbabwe where economic challenges have affected the viability of phosphate rock mining and led to the closure of the mine twice, there is need to evaluate if there have been any significant changes in the quality of the phosphate rock. The current DPR concentrate contained 11% more apatite and about 50% less calcite and other gangue minerals compared to previously reported mineralogical modal concentrations for DPR. Total P was found to have increased by 2% from previously reported figures to 16.5 % by weight and the DPR had fluoride content of 2%. Previously unreported, the cadmium content was found to be 0.16 mg kg^{-1}. The reactivity of the DPR was similar to previously reported values, at 2.1, 1.8 and 0.88% (w/w) in 2% citric acid, 2% formic acid and neutral ammonium citrate respectively. As a result of this, DPR has low potential for direct application without modification. We conclude therefore that the apatite mineralogy of the ore being currently mined has not significantly changed in the past 25 years while the beneficiation process has improved.

3.1 Introduction

The Dorowa phosphate rock (DPR) is an igneous phosphate rock (PR) that is currently the only commercially mined PR in Zimbabwe for fertiliser production since 1965. Since this time, production steadily increased up to the early nineties, where it averaged about 400 tonnes per day translating to 130,000 tonnes per year (Barber, 1991; Van Kauwenbergh, 1991). While production peaked from 1993-1995, it has been decreasing since 1996 (Figure 3.1) and the PR mine has suffered closure many times. This is because of national economic challenges that have affected Zimbabwe and resulted in poor maintenance of national infrastructure such as transport systems and electrical power supply. Phosphate rock mining operations at the Dorowa mine were temporarily suspended in the years 2007 and 2012. The mining operator cited liquidity challenges and lack of PR uptake by Zimbabwe Phosphate Industries Ltd (Mugabe, 2012). Between 2013 to 2015 annual production has been at its lowest in the past 25 years.

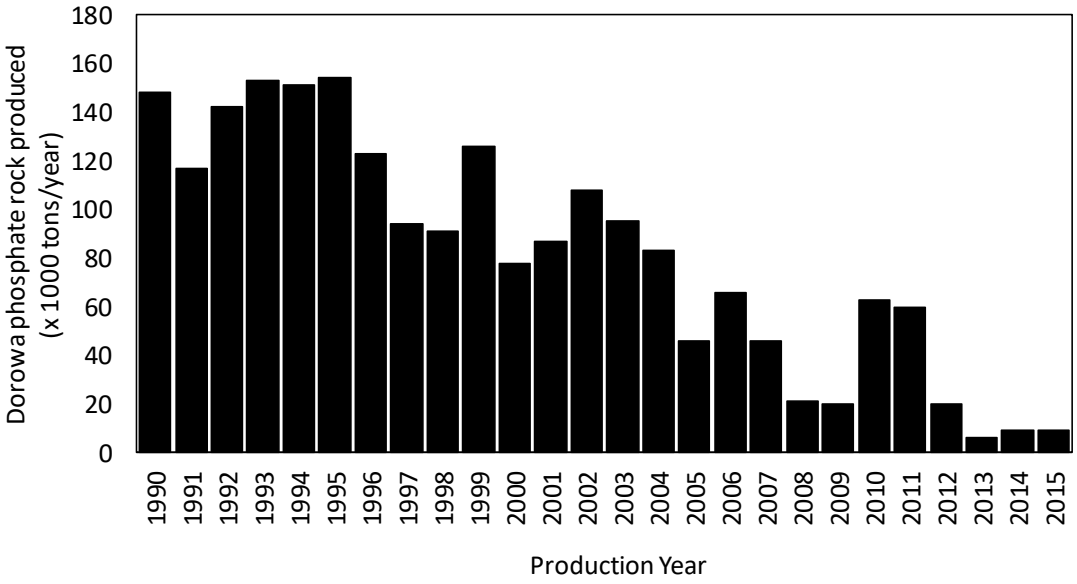

Figure 3.1 Annual production of DPR in Zimbabwe from 1990 to 2015. (Data compiled from (Mobbs, 2016; Mobbs, 2011; Mobbs, 2009; Mobbs, 1999; Barry, 2017; Coakley, 2000; Mobbs, 1994)

Lack of investment funds to develop or replace infrastructure required for mining and beneficiation of PR are cited as major hindrances (van Straaten, 2002; Mobbs, 2013). Poorly maintained mining infrastructure is likely to influence the characteristics of the rock concentrate produced. An early publication by McClellan and Notholt (1986) gives some characterisation details of DPR that was produced at the time. More comprehensive chemical characterisation data were based on an unpublished report by the International Fertiliser Development Centre (IFDC 1987). However, this work did not include an analysis of most of the rare earth elements (REEs) in the rock. Papers published after that work have quoted this same data (Barber, 1991; Van Kauwenbergh, 1991).

Agricultural researchers working with DPR have quoted the analysis data reported by Barber (1991) or Van Kauwenbergh (1991), and have not determined the chemical charateristics of their sample. Barber (1991) reported a DPR sample with 14.45% total P (TP) and low solubility in neutral ammonium citrate (0.8% w/w) with a calcite content of 8%. The DPR was classed as an un-reactive PR not suitable for direct application and suitable only for manufacturing into soluble P fertiliser such as single superphosphate (SSP). Since then, significant changes in the Dorowa mine have precipitated the need for a more comprehensive and up to date characterisation of the DPR.

The characteristics of the current DPR (circa June 2016) will depend on the dikes/veins being mined and the current beneficiation process and blending regime. Mineralogy may change as the concentration of various gangue minerals varies with source. Although (Meck *et al.*, 2011) found that most rocks around the Dorowa mine site were associated with As, Be, Cd, Co, Cu, Ni, Sb, Se and Zn, they highlighted that the metal content in rocks with fluorapatite was lower than those with hydroxyapatite. Published information

on content of these trace metals in the actual DPR is currently not available. The acidulation industrial processes employed to manufacture phosphate fertilisers can lead to high concentrations of bio-available toxic elements in both products and wastes (Rentería-Villalobos *et al.*, 2010). Most REEs and impurities like Cd are known to directly enter the wet process phosphoric acid and end up eventually in the final phosphate fertiliser (Nazari *et al.*, 2005; Liang *et al.*, 2017).

The accumulation of Cd in agricultural soils because of phosphate fertilisation may lead to its uptake and accumulation in consumed foods that may cause kidney diseases (Roberts, 2014). The potential of uptake is increased due to its persistence in soils after continuous fertilisation with high Cd containing fertilisers. Cadmium is known to accumulate mainly in liver and kidneys of grazing animals through herbage ingestion (Loganathan *et al.*, 2003). It is therefore worthwhile to check the levels of non-nutritional impurities in phosphate rocks used to manufacture fertilisers to avoid long-term contamination of soils.

The present study seeks to re-assess the physical and chemical characteristics of the current DPR, prior to its use as a feedstock for fertiliser manufacture and agronomic evaluation. In addition, this publication provides a reference for current researchers requiring chemical analysis of DPR, that includes for the first-time rare-earth elements (REE) and thermal stability of the PR.

3.2 Materials and Methods

3.2.1 Samples

A composite sample of the DPR was obtained from Dorowa mine in Buhera, Zimbabwe. The composite sample was extracted from at least ten positions in the pile awaiting transportation for acidulation in June 2016. For comparisons, samples of Sechura, Jordan and Arad PR were obtained from Massey University, Palmerston North fertiliser store used for teaching purposes. Sub-samples were obtained using a stainless-steel riffler and finely ground to less than 150 µm using a RockLabs® tungsten carbide ring mill. Finely ground DPR was used for chemical content analysis, crystalline phases identification and reactivity characterisation (This chapter, section 3.2.3 and 3.2.5)

3.2.2 Determination of particle size distribution

The particle size distribution of 'as received' and ground DPR was analysed by laser diffractometry using a Partica LA-950V2® laser particle size distribution analyser. An initial 3-minute ultrasonic mixing phase was employed, and sample analysis was done in triplicate, each consisting of an average of three readings. 'As received' samples were riffled down to about a gram (g), each using a sample splitter before analysis to minimise sampling error caused by particle settling.

3.2.3 Determination of DPR mineralogy and thermal stability

Analysis of crystalline phases in the DPR was conducted using powder x-ray diffraction analysis carried out on a Rigaku Spider x-ray diffractometer with Cu Kα radiation (Rigaku MM007 microfocus rotating-anode generator), monochromated and focused with high-flux Osmic multilayer mirror optics, and a curved image plate detector. Ground DPR was fixed to a mount with a minimum amount of fomblin oil. Obtained data was

imported and analysed by running Sleve+ software through the International Centre for Diffraction Data (ICDD), PDF-2 2018® database.

Thermo-gravimetric analysis was performed to quantify mass changes during heating and determine stability properties and points of reaction on a NETZCH STA 449 F1 Jupiter® gravimetric thermal analyser. The atmosphere for analyses consisted of a flow of N_2 at 40 ml/min (protective flow for the balance) and air at 50 ml/min. About 13-15 mg of sample were weighed into pre-weighed platinum crucibles and placed in a high temperature rhodium furnace together with a reference crucible without a sample. Heating was done at 20 ºC/min beginning at 60 and reaching 1200 ºC.

3.2.4 Determination of elemental content

Elemental content of the DPR was measured using X-ray fluorescence (XRF). Major elements were analysed using fused glass beads to minimise matrix effects and minor elements were analysed in pressed powder pellets. Fused glass beads were made by mixing 0.8 g of sample with 8.0 g of X-ray flux (57% lithium tetraborate and 43% of lithium metaborate) and fusing in platinum crucibles in an xrFuse2®. Pressed powder pellets were made by adding to the sample a few drops of a PVA binding solution (polyvinyl alcohol powder, 16% (v/v) ethanol). The mixture was then placed in aluminium cups and 15-20 t of pressure was applied for 40-50 seconds using a FluXana® powder press. Pressed powder pellets and glass beads were analysed on a Bruker S8 Tiger X-ray fluorescence machine. Certified reference materials Oreas 24b and Oreas 24c from Ore Research and Exploration (ORE) were used as checks. Total carbon (C) content was determined after weighing 150 mg of ground rock into tin foil and analysed on the Elementar (Elementar, Vario MACRO, Germany). The calcite content was calculated assuming all C in the DPR was contained in $CaCO_3$.

Total P was determined after acid digestion of 2.5 g of sample in 25 ml of boiling HNO_3: HCl (1:4). Digests were diluted to 50 ml with deionised water and P concentration determined by UV-VIS spectrophotometry by measuring the absorbance of a phospho-vanado-molybdate complex at 420 nm according to Fertmark (2016). Fluoride (F) content was measured using a selective ion electrode after extracting the F in 2.4 M HCl and 10% NH_4Cl (Fertmark, 2016). The amount of F in the samples was calculated using a formula generated from a graph of standard concentrations against the voltmeter reading in mV. Cadmium content was determined after digestion in boiling concentrated HNO_3 (69%) (1g rock/10 ml acid) for 4 hours. Digests were diluted with deionised water to 25 ml and Cd content was determined using a graphite furnace atomic absorption spectrophotometer (GFAAS). Accuracy of obtained values was evaluated by including a boiled concentrated HNO_3 as a method blank, previously analysed Sechura PR as an internal check standard and spiked samples to check and correct for matrix effects on emission spectra.

3.2.5 *Determination of reactivity indices*

The solubility of P in PR samples was determined by standard methods of extraction (Mackay *et al.*, 1984) in 2% citric acid, 2% formic acid and neutral ammonium citrate. Extractions in citric and formic acids were conducted at room temperature (25 ^{0}C) on an end to end shaker for 30 minutes. Extractions in neutral ammonium citrate were conducted on a shaking water bath (Grant® SS40-1) at 65 ^{0}C for 1 hour (EU, 2003). The suspension was centrifuged at 10 000 rpm for 5 minutes on a Thermo Scientific® RC 6+ centrifuge and immediately filtered on a dry pleated Whatman No. 42 filter paper. Another sequential extraction was performed to the rock residue and analysed for P concentration as above.

3.3 Results and Discussion

3.3.1 Particle size distribution of the DPR

In its 'as received' state, DPR has been milled at the mine before dispatch and has a normally distributed particle size distribution with about 94% of particles less than or equal to 250 µm (Figure 3.2). Prior to total element analysis, sub-samples were ground further using a ring grinder (RockLabs) leaving all particles less than 100 µm and 95 % of particles equal or less than 31.3 µm in diameter.

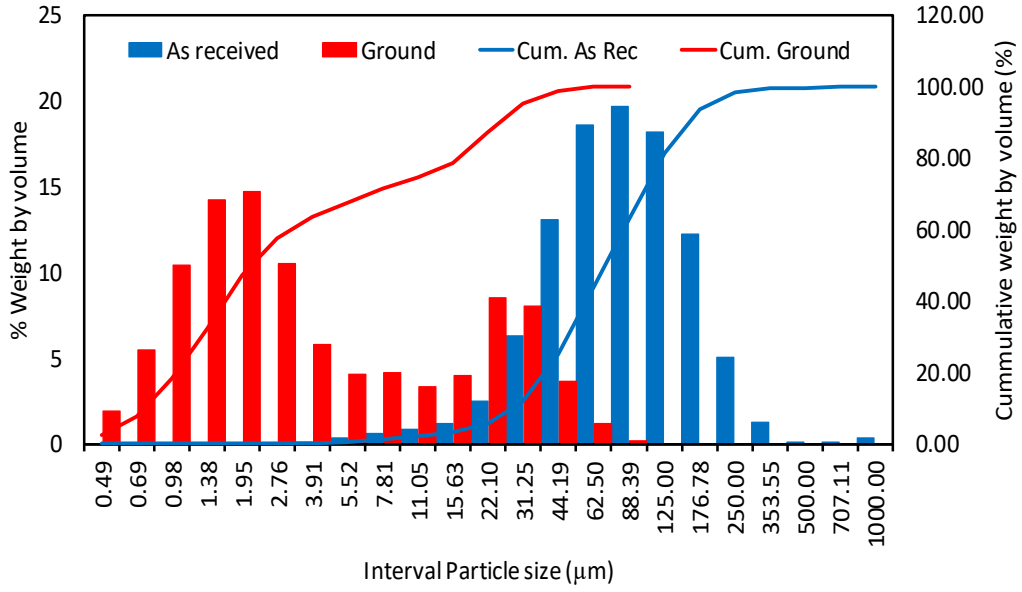

Figure 3.2 Particle size distribution (% weight by volume) of the DPR as received from mine and when ring ground

3.3.2 Mineral Phases in the DPR

X-ray diffractogram data showed that the current DPR consists mainly of hydroxy-fluorapatite and calcite ($CaCO_3$) (Figure 3.3). Contrary to the mineralogical analysis earlier reported by Barber (1991), magnesioriebeckite ($Na_2[(Mg;Fe^{2+})_3Fe^{3+}{}_2]Si_8O_{22}(OH)_2$) and aegirine-augite ($Ca_{0.75}Na_{0.25}Mg_{0.5}Fe^{2+}{}_{0.25}Fe^{3+}{}_{0.25}(Si_2O_6)$) were not

identified in the current DPR. Comparing the X-ray diffractograms obtained in this study (Figure 3.3) and the one reported by Barber (1991) shows that the calcite peaks obtained in this study are considerably smaller than those reported by Barber (1991).

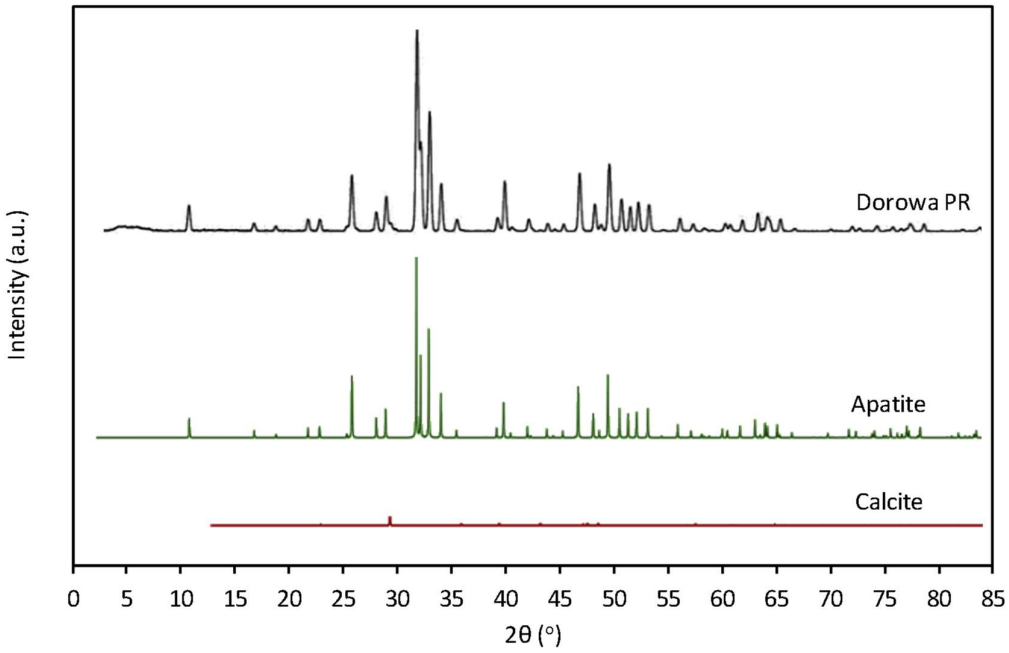

Figure 3.3 X-ray diffractogram of the DPR obtained using Cu $K_{\alpha 1}$ radiation.

This is because the amount of calcite in the PR analysed in this study (3.5%, calculated from % C in Table 3.1) is less than half of the one earlier reported (8%). Improvements in the mining and or beneficiation processes might have led to improved removal of silicate minerals and calcite in the final product.

3.3.3 Thermal stability of the DPR

When DPR is heated in air up to 1200 ºC it loses about 1.49% of its total mass. A small mass change of 0.17% at ≤ 500 ºC suggests that the PR has very little adsorbed chemical water and organic matter. The only major thermal event observed during heating resulted in a mass loss of 1.21% that corresponded with an endothermic differential scanning

calorimetric (DSC) peak at 675 °C (Figure 3.4). This peak and mass loss are likely due to calcite decomposition which liberates CaO and CO_2 gas. Complete decomposition of calcite will result in a 44% reduction in mass of the calcite (as remaining CaO). For a rock containing 3.5% calcite complete calcite decomposition will in theory result in a mass loss of 1.54%. There is reasonable agreement between the mass loss measured thermogravimetrically and that estimated from calcite content. From 900 to 1200 °C there is a slight and gradual mass loss of 0.28% that might be due to defluorination and or de-hydroxylation reactions going on at a very slow rate.

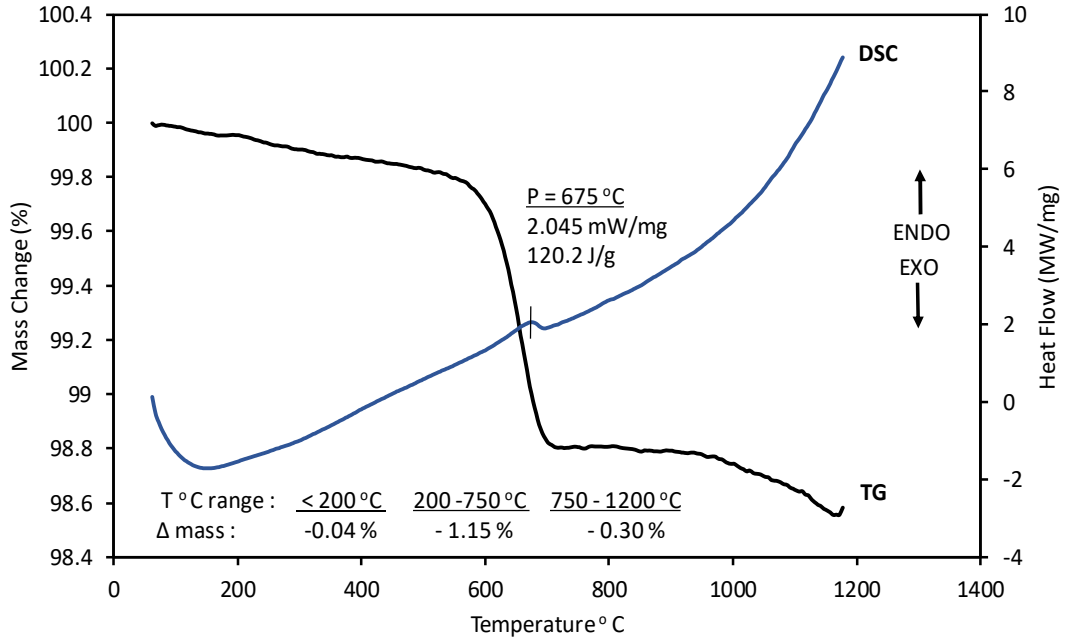

Figure 3.4 Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves of the DPR when heated in air

3.3.4 Elemental composition

The Ca content of DPR was 37.12%, which is slightly more than the 35.93% previously reported by Barber (1991) but in the range of other igneous PR concentrates such as Phalaborwa and Bou Craa (Table 3.1).

Table 3.1 Elemental content of the DPR. Results are compared to other PRs in the literature.

	Igneous					Sedimentary	
	Dorowa[a], Zimbabwe			Phalaborwa[b*], South Africa	Evate[c], Mozambique	Bou Craa[b**], Morrocco	Hazm Al – Jalamid[d], Saudi Arabia
Element	1	2	3				
Ca (%)	37.11	37.19	37.02	37.16	36.29	37.09	36.05
P (%)	16.7	16.5	16.4	15.93	23.97	15.97	9.27
Si (%)	1.14	1.16	1.15	0.56	2.02	2.11	1.30
C (%)	0.40	0.43	0.43	1.15	n.d.	0.50	n.m.
Na (%)	0.36	0.36	0.37	0.03	n.m.	0.18	0.20
Sr (%)	0.31	0.31	0.31	n.m.	0.26	0.03	0.55
Mg (%)	0.30	0.31	0.31	1.45	n.d.	0.04	1.42
Fe (%)	0.97	0.99	0.97	0.38	0.74	0.1	0.18
Al (%)	0.17	0.16	0.15	0.07	0.77	0.23	0.21
K (%)	0.03	0.03	0.03	0.03	0.33	0.12	0.03
S (%)	0.02	0.02	0.02	n.m.	n.d.	0.18	n.m.
Ti (%)	0.02	0.02	0.02	n.m.	0.12	0.02	n.m.
Mn (%)	0.04	0.04	0.04	n.m.	0.05	n.m.	0.0008
Ba (%)	0.03	0.03	0.03	n.m.	0.20	n.m.	0.01
Ce (mg/kg)	172	167	168	n.m.	n.m.	n.m.	7.28
Cl (mg/kg)	119	119	113	300	1254.00	400	n.m.
Zr (mg/kg)	88	99	97	n.m.	51.00	n.m.	14.01
Y (mg/kg)	95	94	94	n.m.	152.77	n.m.	36.96
La (mg/kg)	87	96	90	n.m.	n.m.	n.m.	n.m.
Nd (mg/kg)	82	84	84	n.m.	n.m.	n.m.	7.98
Sc (mg/kg)	58	58	58	n.m.	n.m.	n.m.	n.m.
V (mg/kg)	29	28	29	n.m.	120	n.m.	n.m.
Cu (mg/kg)	20	20	20	n.m.	17.00	n.m.	n.m.
Th (mg/kg)	17	16	16	n.m.	n.m.	n.m.	n.m.
Zn (mg/kg)	12	11	12	n.m.	36.00	n.m.	n.m.
As (mg/kg)	4	6	5	n.m.	36.90	n.m.	n.m.
Nb (mg/kg)	6	4	5	n.m.	n.m.	n.m.	n.m.
Mo (mg/kg)	5	5	5	n.m.	9.70	n.m.	n.m.
Pb (mg/kg)	3	4	5	n.m.	26.00	n.m.	n.m.
U (mg/kg)	4	4	4	n.m.	n.m.	n.m.	88.7
Cs (mg/kg)	3	1	1	n.m.	n.m.	n.m.	n.m.
Sn (mg/kg)	n.d.	n.d.	3	n.m.	n.m.	n.m.	n.m.
Ni (mg/kg)	1	n.d.	1	n.m.	58.00	n.m.	n.m.
Sb (mg/kg)	n.d.	n.d.	1	n.m.	n.m.	n.m.	n.m.
Cr (mg/kg)	n.d.	n.d.	n.d.	n.m.	129.00	n.m.	68.42
Co (mg/kg)	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.
Ga (mg/kg)	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.
Rb (mg/kg)	n.d.	n.d.	n.d.	n.m.	21.60	n.m.	n.m.
Tl (mg/kg)	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.

[a]This study, [b](Van Kauwenbergh, 2006), [c](Rafael *et al.*, 2018), [d](Khater *et al.*, 2016), [*] PALPHOS 86S concentrate, [**]80% BPL concentrate, n.d. - not detected, n.m. - not measured or not reported

Values obtained for Fe, Al, Mg and K were generally half of what was reported by Barber (1991). Confidence in our analysis from certified reference sample values whose variance with reported values was within 2%, would suggest the elemental variance lies in sample itself. This variance is likely because the current sample has less gangue minerals. The current DPR has an estimated 89% apatite content, 3.5% calcite content and about 7.5% other gangue minerals compared to previously reported modal concentrations of 78% apatite, 8% calcite and 14% other gangue minerals (Barber, 1991).

While the amount of Fe in the current DPR is lower than previously reported, it is still high when compared to other igneous PRs such as Phalaborwa and Evate (Table 3.1). Contrary to a previously reported $Fe_2O_3 + Al_2O_3 + MgO$: P_2O_5 ratio of 0.13, the current DPR sample has a $Fe_2O_3 + Al_2O_3 + MgO$: P_2O_5 ratio of 0.056 making it suitable for chemical processing/ acidulation. During acidulation, Fe, Al and Mg react with either or both P and ammonia chemically limiting the acid formulation (Yarnell, 1987). Lower Fe Al, and Mg contents mean that issues to do with the formation of insoluble Fe and Al phosphates during the stage of concentration of wet process acid may not arise. The DPR has low sulphur content (0.02%) compared to PRs like Bou Craa (0.18% S). As a result, odour assessment trials for potential production of poisonous and corrosive H_2S gas during acidulation may not be needed.

The concentrations of Sr, Zr and Ce in the analysed DPR sample were 3132, 94.67 and 169 mg/kg respectively, showing reduced concentrations from previously reported concentrations of 4397, 148 and 269.25 mg/kg respectively (Barber, 1991). We speculate that a considerable amount of Sr, Zr and Ce were present in the gangue minerals and their improved removal in the current sample led to a reduction of these elements by about

30%. The current DPR contains low Ba (0.03%) compared to Evate PR from Mozambique that contains 0.2% Ba (Rafael *et al.*, 2018). Rentería-Villalobos *et al.* (2010) notes that PRs of igneous origin usually contain high amounts of Ba that is further concentrated by up to 650% in phosphogypsum during acidulation and about 21% of the toxic Ba can exist in the bio-available fraction. It is unlikely that the low content of Ba in DPR will give problems in the final products.

Concentrations of rare earth elements (REEs) in DPR was in the order Ce > Y ≈ La ≈ Nd and ranged between 83 and 169 mg/kg. These are consistent with those in Nash (1984), who reported higher substitutions between REE and Ca^{2+} in apatite minerals when the crystal ionic radii of the REE was closest to that of Ca^{2+}. In this case, the high Ce content is likely because Ce^{3+} has a crystal ionic radius of 115 pm which is similar to that of Ca^{2+} of 114 pm. Cerium content in DPR was about 20x more than that in a sedimentary Hazm Al Jalamid PR reported by Khater *et al.* (2016). During acidulation, most of the REEs in the phosphoric acid phase eventually end up in the phosphate fertiliser and their accumulation in soil due to fertiliser application can be toxic to soil macrofauna (Liang *et al.*, 2017). Analysis of concentrations of REEs found to be in relatively higher concentrations such as Ce, Y, La and Nd in the final produced phosphate fertilisers is recommended. Other elements such as, Nb, Mo, Pb, U, Cs, Sn, Ni, Sb were low, ranging from 5 to 0.3 mg/kg.

Cadmium and F contents in the DPR were found to be low at 0.16 mg kg^{-1} and 2% respectively (Table 3.2). Cadmium in the DPR was comparable to other igneous PR such as Phalaborwa and Kola. Fluoride content was more than that reported by Barber (1991)

who reported it to be 1.6%. The slight increase in F could be because the current rock contains more hydroxy fluorapatite.

Although important, there has been no publication about the Cd content of the DPR. Different countries have set limits for Cd in fertiliser, for example, limits of mg Cd/kg of P fertiliser with about 19.62% P range from 7.9 to 400 mg Cd/kg depending on the country (Roberts, 2014). Current fertiliser regulations in Zimbabwe do not specify limits for Cd and F content of fertilisers. The current European limit for Cd is 26.16 mg Cd/kg P with plans to reduce it to 8.72 mg Cd/kg P (Kratz *et al.*, 2016). Single super phosphate (8.5% P) made with the DPR would contain an estimated 0.082 mg Cd/kg fertiliser (0.96 mg Cd/ kg P). Compared to reactive PRs analysed in this study, Cd content in DPR was the lowest and both the concentrate and final fertiliser would pass Cd limits in other countries. The low levels of total F and Cd in DPR indicate that it is unlikely to significantly increase F and Cd in soils (Loganathan *et al.*, 2003).

Table 3.2 Cadmium and fluoride content of the DPR in comparison to some selected PRs analysed in this study and in the literature.

Phosphate rock	mg Cd /kg PR	mg Cd/kg P	% F
Igneous			
Dorowa	0.16 ± 0.00	0.97	2.01 ± 0.00
Phalaborwa 80M [a, b]	0.15	0.9	2.1
Kola[a]	0.15	0.9	n.m.
Sedimentary			
Sechura	5.34 ± 0.25	40.45	3.40 ± 0.00
Jordan	2.69 ± 0.08	18.18	4.05 ± 0.11
Arad	3.20 ± 0.84	21.92	4.56 ± 0.06
Bou Craa[a, b]	35	220	3.93

[a] (Appleton, 2002), [b] (Van Kauwenbergh, 2006), numbers after ± are standards errors of means (n=3), n.d. means not measured or reported

3.3.5 Phosphate content and reactivity indices

The total P in the DPR analysed in this study was 16.5% by weight when measured by wet chemistry (Table 3.3). This is more than what previous studies (Govere *et al.*, 2003; Govere *et al.*, 2005; Smalberger *et al.*, 2006; IFA, 2013) have reported being in the range 14.39- 14.52 % P. It is interesting to note that, although not reported as analytic results, van Straaten (2002) reports that the P content of the DPR produced in the year 2000 contained about 16.13% P. The amounts of P soluble in 2% citric acid (2.1%) and formic acid (1.81%) were slightly more than those reported by Smalberger *et al.* (2006) and IFA (2013) of 1.83% and 1.66% citric and formic acid soluble P respectively.

Table 3.3 Total P and its solubility in neutral ammonium citrate, 2% formic acid and 2% citric acid of ground DPR compared to other selected phosphate rocks.

Phosphate Rock	% P (w/w)	NAC Soluble P (%) *		Formic Soluble P (%) *		Citric Soluble P (%) *	
		1st extraction	2nd extraction	1st Extraction	2nd extraction	1st extraction	2nd extraction
Igneous							
Dorowa	16.5 ± 0.09	0.46 ± 0.01	0.42 ± 0.01	1.81 ± 0.02	2.19 ± 0.004	2.09 ± 0.04	2.21 ± 0.01
Phalaborwa[a]	16.1	0.3	0.7	n.d.	n.d.	1.6	n.d.
Udaipar[b]	18.3	0.52	0.49	0.93	n.d.	1.67	n.d.
Sedimentary							
Sechura	13.2 ± 0.21	3.07 ± 0.04	2.41 ± 0.01	8.01 ± 0.09	3.73 ± 0.06	6.19 ± 0.01	3.72 ± 0.05
Jordan	14.8 ± 0.07	1.37 ± 0.01	1.22 ± 0.03	6.89 ± 0.01	4.98 ± 0.09	4.74 ± 0.03	3.39 ± 0.03
Arad	14.6 ± 0.03	1.55 ± 0.03	1.87 ± 0.01	8.48 ± 0.09	5.58 ± 0.05	5.10 ± 0.21	4.34 ± 0.03
Minjungu[a,]	13.0	3.4	3.7	n.d.	n.d.	6.3	n.d.

[a](Smalberger *et al.*, 2006), [b](Basak, 2019), n.d. not reported, * % w/w, numbers after ± are standards errors of means (n=3)

However, the obtained citric acid soluble P values were slightly less than the 2.4% reported by Govere *et al.* (2005). The P solubility in neutral ammonium citrate (NAC) of DPR was 0.88%, which was slightly more than the 0.65% reported by IFA (2013) and slightly less than the 1.2% P reported by Smalberger *et al.* (2006). These differences are

expected to result from differences in the beneficiation and blending process. The solubility of the current DPR is similar to that of other igneous PRs such as Phalaborwa and Udaipar reported by Van Kauwenbergh (2006) and Basak (2019). Sedimentary PRs such as Sechura and Minjungu have about 6x more NAC soluble P and about 3x more citric acid soluble P compared to the igneous DPR, Phalaborwa and Udaipar PRs. The low P solubility values for the DPR make it suitable for manufacturing soluble P fertilisers (Bolan *et al.*, 1990) but of limited agronomic value as a direct application PR (Diamond, 1979; Rajan *et al.*, 1992). For DPR, the amount of soluble P in each extractant in the first and second extractions were comparable whereas other analysed rocks generally had less soluble P in the second extraction (Table 3.3). This suggests that the DPR might have good potential to release P in sequential weak acid leaching systems.

An analysis of P in different particles sizes of DPR revealed that P is evenly distributed across the particle sizes (Table 3.4). The total P measured in particles below 250 µm averaged 16.68% P and this particle size range constituted 98% of the concentrate (Table 3.4). Particles greater than 250 µm were not analysed for P because insufficient quantities were obtained. However, it is hypothesised that these particles might have significantly less P content, but it will not make economic sense to target their removal.

Table 3.4 Phosphate distribution in different size fractions of the DPR.

DPR particle size fraction	% by weight	% P (w/w)
75 µm > x	41	16.62 ± 0.11
75 µm < x < 150 µm	41	16.69 ± 0.28
150 µm < x < 250 µm	16	16.72 ± 0.24
250 µm < x	2	n.d.

Numbers after ± are standards errors of means (n=3), n.d. means not determined

3.4 Conclusions

The DPR analysed in this study shows marked differences in mineral phase abundances and has about 89% apatite and 3.5% calcite. Changes in mineral phase abundances are further confirmed by increased P content from 14.5 to 16.5% P and reduced contents of elements such as Si, C, Fe, Al and Mg when compared to an earlier report by Barber (1991). The solubility of DPR in 2% citric acid, 2% formic acid and neutral ammonium citrate has remained largely the same. It is speculated that there have been improvements in the mining and beneficiation process, or the current grade of the ore has a higher apatite content. The low P solubility of the current DPR means that it has very low potential for agronomic use in its 'as received' state. The low levels of total F and cadmium in DPR indicate that there will be low, or no soil contamination issues associated with F and Cd in final fertiliser products.

The outcome of this chapter fulfils the first objective of the thesis of characterising a more recent sample of the DPR.

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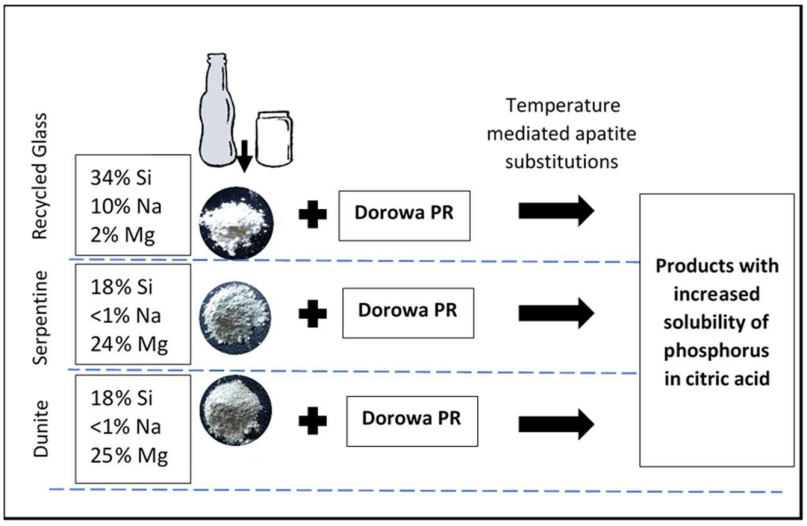
CHAPTER 4

INCREASING PHOSPHORUS SOLUBILITY BY SINTERING IGNEOUS DOROWA PHOSPHATE ROCK WITH RECYCLED GLASS

Results from Chapter 3 expressed that there was need to modify the Dorowa PR to improve its agronomic value. However, more economic alternatives to sulphuric acid acidulation are required because of the low foreign currency reserves in Zimbabwe that discourage sulphur imports (Chapter 2). In this chapter, the potential of using recycled glass as an economic silicate source for temperature mediated isomorphous substitutions which could improve the agronomic value of the Dorowa PR is evaluated.



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Abstract

The lack of low-cost phosphorus (P) fertilisers is a major limitation for food production on Zimbabwe's many smallholdings. A thermally fused magnesium phosphate could be manufactured from the local Dorowa phosphate rock (DPR) but would be expensive because of the high cost of required additives and energy. This paper investigates the P solubility of mixtures of igneous DPR with either recycled glass or magnesium silicates, before and after thermal alteration at sub-fusion temperatures. The thermal behaviour and chemical transformation of DPR and various additives were investigated by thermo-gravimetric and differential scanning calorimetric analysis and X-ray powder diffraction. Thermal transformation of DPR + serpentine and DPR + dunite mixtures resulted in decomposition of calcite, kellyite, lizardite, and chrysotile present in the original mixtures, and recrystallisation of dehydroxylated metachrysotile to forsterite. The final products of air cooled DPR + glass mixtures sintered at 900 ºC contained iron silicate ($Fe_2(SiO_4)$), wollastonite ($CaSiO_3$), quartz (SiO_2), muscovite and hydroxy-fluorapatite. Compared to the unamended DPR, thermal alteration of DPR + glass mixtures at 900 ºC led to a 62, 73, and 44% increase of citric soluble P when mixed at 1:2, 1:1, and 2:1 (DPR/ glass) respectively. This increase in the citric soluble P content increases the agronomic value of the DPR and is likely the result of substitution of PO_4^{3-} in hydroxy-fluorapatite by SiO_4^{4-} and or Mg^{2+}/Na^{+} for Ca^{2+} and Fe^{2+}.

4.1 Introduction

Agricultural phosphorus (P) shortages are widespread in Zimbabwe smallholder farming areas. Most smallholder farmers apply suboptimal fertiliser rates to the already severely nutrient-deficient soils, limiting expected yields and making sustainable production difficult to attain (Tumbure *et al.*, 2013; Soropa *et al.*, 2018). The cost of phosphate fertiliser is usually beyond the reach of many of these farmers, since all the phosphate rock (PR) that is mined in Zimbabwe is processed via the wet acid pathway, which uses expensive imported elemental sulphur. In addition to high acidulation costs, transport costs significantly increase the price of the final product. Indigenous PRs can be an alternative fertiliser option in marginalised smallholder farming areas. However, the bio-availability of P present in PR strongly depends on the rock's chemical, physical, and mineralogical/crystallographic properties which affects the PR's agronomic potential (Aydin *et al.*, 2009; IFA, 2013). Since the PR's apatite structure allows numerous substitutions, the type of substitutions present strongly affect their physicochemical properties (Chihi *et al.*, 2016).

Dorowa PR (DPR) is an igneous PR from Buhera district in Zimbabwe. It has a coarse crystalline nature that lacks internal surfaces, rendering it much less reactive (Govere *et al.*, 2003; Tumbure *et al.*, 2019). While it is used to manufacture phosphate fertilisers through the wet acid process pathway, alternative low-cost options for its use, which may be more suitable for small-scale impoverished farmers, are limited (Tumbure *et al.*, 2020). Previous studies have shown that unmodified DPR has very little agronomic value when directly applied. For example, Govere *et al.* (2003); Govere *et al.* (2005) reported that the direct application of DPR at 150 mg P kg $^{-1}$ soil was ineffective in improving biomass and P uptake by maize and ryegrass, respectively. Nezomba *et al.* (2007) also reported no

significant improvement in the total biomass of legume and grass species in fallows compared to unfertilised fallows after the direct application of DPR at a rate of 26 kg P ha $^{-1}$, in Masvingo, Zimbabwe.

Thermally altered phosphates made from un-reactive igneous PRs can be a viable option for smallholder farmers. However, thermal phosphate production is seldom economically feasible because of the high energy requirement. Fused magnesium phosphates are produced by heating mixtures of PR with olivine/serpentine to 1500 – 1600 ^{o}C, and Rhenania phosphates are produced when a PR, soda ash, and silica mixture is heated between 1200 – 1300 ^{o}C (Bolan *et al.*, 1993; van Straaten, 2002; Watti *et al.*, 2016; Dwivedi and Gupta, 2006). Additives used in fused magnesium phosphate production aid in collapsing the apatite crystal lattice by encouraging defluorination and forming a eutectic system that reduces the fusion temperature (Dwivedi and Gupta, 2006; Ranawat *et al.*, 2009). However, the process consumes a lot of water, which is used to quench the melt to stop re-crystallisation and fix the remaining fluorine in a vitreous phase (Ando, 1987; Cekinski and DaSilva, 1998; da Silva and Kulay, 2005). These products have a high P solubility in 2% citric acid, which indicates the ability of thermally produced P fertilisers to provide plant available P in the mid- to long-term (Vaclavkova *et al.*, 2018; Möller *et al.*, 2018).

When PR is mixed with silicates, heating can result in isomorphous substitution of PO_4^{-3} by SiO_4^{-4} and SO_4^{-2} (Knubovets *et al.*, 1997; Kaljuvee *et al.*, 2019). Studies by Jamil *et al.* (2020) report substitution of PO_4^{3-} with the SiO_4^{4-} group and the resultant loss of OH^- in order to compensate for the extra negative charge of the SiO_4^{4-} after clay minerals and synthesised hydroxyapatites were sintered at 900 ^{o}C. When Rhenania phosphate is

produced, Na can substitute for Ca in the apatite structure as fluoride is driven off, as indicated by the general equation 4.1 (Bolan *et al.*, 1993):

$$Ca_{10}(PO_4)_6F_2 + 4Na_2CO_3 + 4SiO_2 \xrightarrow{\Delta} 6CaNaPO_4 + 2Ca_2SiO_4 + 2NaF + 4CO_2 \quad (\mathbf{4.1})$$

Studies by Watti *et al.* (2016) on the thermal treatment of Syrian sedimentary PR with sodium carbonate showed that the optimum mixing ratio for maximum citric solubility was 40 % of sodium carbonate by mass of phosphate rock, sintered at 1100 ºC. Other studies by Rautaray *et al.* (1995), using Indian PRs, indicated that thermally altered PR products, with a citric soluble P of at least 50 %, could be prepared by sintering PR + Na_2CO_3 mixtures in ratios of 2:1 (PR/Na_2CO_3 w/w) and heated at 900 ºC.

Thermally produced phosphates provide a viable agronomic option if they can be produced cheaply using less energy, water, and alternative low-cost addition agents. The possibility of using sintering temperatures less than 1000 ºC means that existing brick firing kilns can be used on a small scale in rural communities to produce sintered phosphate fertilisers, as well as bricks. Transport costs can also be greatly reduced because communities near phosphate mines, such as the Dorowa mine in Buhera, would only need to transport feedstock for a short distance (50 km radius) as opposed to purchasing and transporting single super phosphate (SSP) from Harare (250 km by road), where the PR is currently acidulated.

This chapter investigated the possibility of providing a soluble P source, by thermal alteration of the DPR through sintering with a range of relatively inexpensive silicate sources.

4.2 Materials and methods

4.2.1 Samples

The DPR was obtained from Dorowa mine in Buhera, Zimbabwe (19° 03' 47" S, 31° 45' 45" E). Serpentine and dunite (both sources of SiO_2 and Mg) held in the Massey University store, were originally obtained from New Zealand deposits at Pio Pio (38° 32' 40'' S, 175° 01' 02" E, Rorison Mineral Developments Ltd.) and Greenhills quarry complex (46° 33' 00'' S, 168° 15' 54" E) respectively. Serpentine minerals were selected because a source, (The Mashava Igneous complex) exists, < 100 km from the Dorowa communal area in Zimbabwe (Chaumba, 2019). All the rock materials were sub-sampled using a stainless-steel riffle splitter and ground to less than 150 µm using a RockLabs® ring mill. Soda lime glass was obtained by crushing washed clear glass bottles/jars and grinding the material to less than 150 µm.

4.2.2 Determination of thermal behaviour

Thermo-gravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were performed on a NETZCH STA 449 F1 Jupiter® gravimetric thermal analyser to quantify mass changes during heating and to determine stability properties and points of reaction. The atmosphere for analyses consisted of a flow of N_2 at 20 ml min^{-1} (protective flow for the balance) and air at 50 ml min^{-1}. Platinum crucibles were used to hold the samples, and heating was conducted at 20 °C min^{-1} from 60 to 1200 °C.

4.2.3 Sintering experiments

Ground DPR, serpentine, dunite, and soda lime glass were dried in an oven overnight at 105 °C. DPR was then weighed into nickel crucibles followed by additions of serpentine/ dunite/ soda lime glass to give ratios of 1:1, 1:2 and 2:1 (DPR/ silicate mineral, w/w). The

total mass of product in each crucible was maintained at 3 g, and a straight DPR was included as a control. Other controls were also included - these consisted of the straight silicate minerals to check if they were contaminated with P. The samples were then transferred to a Carbolite® muffle furnace and the temperature was gradually raised to either 900 or 1000 ºC, and then maintained for 2 hours. These ceiling temperatures were based on the results of the thermal analysis conducted in the "determination of thermal behaviour" section. The sintered product was then removed from the furnace and left to air-cool. Another sintered set was rapidly quenched by submerging the crucibles in deionised ice water. These quenched samples were then dried in an oven at 105 ºC to a constant mass. All products were then ground to less than 150 μm and stored in screw-cap plastic vials before being analysed.

4.2.4 Elemental analysis

Elemental analysis of starting materials was performed on a Bruker S8 Tiger X-ray fluorescence (XRF) machine. For major element analysis, samples were mixed with a flux of 57% lithium tetraborate and 43% lithium metaborate at 1-part sample to 10-parts flux material. Glass disks (for major element analysis) were made by fusing in a xrFuse2 (XRF Scientific) electric fusion machine. Pressed powder pellets (for trace element analysis) were made by compressing a paste of the sample after mixing with about 20 drops of polyvinyl alcohol powder and ethanol 16% (v/v) solution. Pressure was applied using a Fluxana Vaneox® hydraulic press at 20 t for 1 minute. Certified reference materials, Oreas 24b and Oreas 24c from Ore Research and Exploration (ORE), were used as checks.

4.2.5 Analysis of P solubility and selected elements

Total P was determined after acid digestion of 2.5 g of sample in 25 ml of boiling HNO_3: HCl (1:4). Digests were diluted to 50 ml with deionised water, and P concentration then determined by UV-Vis spectrophotometry by measuring the absorbance of a phospho-vanado-molybdate complex at 420 nm (Hedley *et al.*, 1988; Fertmark, 2016). The solubility of P, both in the raw materials and thermally altered samples, was determined by extraction in 2% citric acid at room temperature (25 ^{o}C) on an end to end shaker for 30 minutes followed by the colorimetric finish described above (Mackay *et al.*, 1984). The amount of P that is soluble in 2% citric acid is used as an index of the plant available P content in PRs (Mackay *et al.*, 1984; Petkova *et al.*, 2014; Kaljuvee *et al.*, 2019; Möller *et al.*, 2018; Tumbure *et al.*, 2020) and fertilisers containing partially soluble and soluble P (Condron *et al.*, 1994). It is an official method for testing fertiliser quality in Zimbabwe, New Zealand, and the European Union (EU, 2003; Fertmark, 2016). Selected citric acid extractants were analysed for solubilised Ca, Mg, Na, Fe and Al using microwave plasma atomic absorption spectrophotometry (MP-AES) on an Agilent® 4200 MP-AE Spectrophotometer. These elements were chosen because of their abundance in the additives and the DPR, and likelihood of association with P that may affect bio-availability in the soil environment (Waclawska *et al.*, 2011). The matrix of the standards was matched to that of the extractants before analysis. For Ca, Mg, and Na analysis, a Cs and Sr solution (ionisation suppressant) was added to achieve a concentration of 1000 mg L^{-1} in both the standards and extractants.

4.2.6 Mineral phase identification

Analysis of crystalline phases in raw materials and final products was conducted using powder X-ray diffraction analysis (XRD) with a Rigaku Spider X-ray diffractometer with Cu Kα radiation (Rigaku MM007 microfocus rotating-anode generator), monochromated

and focused with high-flux Osmic multilayer mirror optics, and a curved image plate detector. Individual samples were fixed to a mount with a minimum amount of fomblin perfluoropolyether oil. Raw data was imported and analysed by running Sleve+ software through the International Centre for Diffraction Data (ICDD), PDF-2 2018® database.

4.2.7 Statistical analysis

Data on citric soluble P were grouped by initial DPR content (33, 50, 67 and 100%) and each group was individually analysed for statistical significance by running a multivariate analysis of variance (MANOVA) in R (version 3.5.0). Least significant differences (LSDs) were used to separate significantly different ($P < 0.05$) means. Before analysis, data was checked for normality using normal QQ residual plots.

4.3 Results and discussion

4.3.1 Elemental content of raw materials

The results of XRF analysis of raw materials are presented in Table 4.1. Compared to soda glass, which had an Fe content of 0.16%, serpentine and dunite had moderately high Fe content at 5.18 and 6.60% respectively, with a possibility of forming insoluble iron phosphates, depending on the chemical speciation of the Fe, during sintering. The Mg content of serpentine and dunite were 23.9 and 24.8%, respectively. This was comparable to values reported by Hanly *et al.* (2005) of 23.1% Mg in serpentine from Pio Pio in New Zealand, and values reported by Chittenden *et al.* (1973) of 23 and 23.4% Mg from serpentine collected from Mossburn and Lee Valley in New Zealand, respectively.

Table 4.1 Elemental composition of raw materials used in the sintering process.

Element	Unit	DPR	Serpentine	Dunite	Soda Glass
Ca	%	37.12 ± 0.05	0.19 ± 0.01	1.17 ± 0.002	6.29 ± 0.002
Mg	%	0.31 ± 0.00	23.88 ± 0.02	24.84 ± 0.01	2.38 ± 0.01
Fe	%	0.98 ± 0.01	5.18 ± 0.01	6.60 ± 0.01	0.16 ± 0.01
Al	%	0.16 ± 0	0.51 ± 0.01	0.93 ± 0.01	0.39 ± 0.004
K	%	0.03 ± 0	0.02 ± 0	0.01 ± 0	0.17 ± 0.003
Na	%	0.37 ± 0	0.06 ± 0.004	0.15 ± 0.002	10.42 ± 0.01
P	%	16.5 ± 0.09	n.d.	0.03 ± 0	0.01 ± 0.001
S	%	0.02 ± 0	0.02 ± 0.001	0.01 ± 0	0.02 ± 0
Si	%	1.15 ± 0.01	17.90 ± 0.02	18.36 ± 0.02	33.58 ± 0.04
Ti	%	0.02 ± 0	0.01 ± 0	0.06 ± 0.002	0.02 ± 0
Cl	mg kg $^{-1}$	117 ± 2	4678 ± 530.35	340.33 ± 30.19	279.33 ± 1.76
Sc	mg kg $^{-1}$	58 ± 0	7 ± 0.58	10 ± 0	6.00 ± 0.00
V	mg kg $^{-1}$	28.67 ± 0.33	28 ± 0.00	34 ± 0.58	5.67 ± 0.33
Mn	mg kg $^{-1}$	391.33 ± 0.88	782.67 ± 2.91	1177.67 ± 9.77	105 ± 0.00
Cr	mg kg $^{-1}$	n.d.	1478.67 ± 46.84	2620.33 ± 29.85	28.33 ± 1.33
Co	mg kg $^{-1}$	n.d.	73.33 ± 0.33	113.33 ± 1.76	6.33 ± 0.33
Ni	mg kg $^{-1}$	0.67 ± 0.33	1623 ± 16.56	1400 ± 16.44	11.33 ± 0.33
Cu	mg kg $^{-1}$	20 ± 0	1.67 ± 0.33	7 ± 0.58	11.00 ± 2.00
Zn	mg kg $^{-1}$	11.67 ± 0.33	42 ± 1.00	44.33 ± 0.88	20.67 ± 0.33
Ga	mg kg $^{-1}$	n.d.	1 ± 0.00	2 ± 0.00	0.67 ± 0.33
As	mg kg $^{-1}$	5 ± 0.58	2 ± 0.00	2 ± 0.00	8 ± 0.58
Rb	mg kg $^{-1}$	n.d.	1.67 ± 0.33	2 ± 0.00	6.33 ± 0.33
Sr	mg kg $^{-1}$	3132.33 ± 8.33	7.67 ± 0.33	23.67 ± 0.88	48.33 ± 1.20
Y	mg kg $^{-1}$	94.33 ± 0.33	0.33 ± 0.33	2.33 ± 0.33	2.67 ± 0.33
Zr	mg kg $^{-1}$	94.67 ± 3.38	8 ± 0.00	10.67 ± 0.33	35.67 ± 0.88
Nb	mg kg $^{-1}$	5 ± 0.58	n.d.	n.d.	0.67 ± 0.33
Mo	mg kg $^{-1}$	5 ± 0	4 ± 0.00	4 ± 0.00	4 ± 0.00
Sn	mg kg $^{-1}$	1 ± 1	n.d.	n.d.	17 ± 2.52
Sb	mg kg $^{-1}$	0.33 ± 0.33	n.d.	n.d.	n.d.
Cs	mg kg $^{-1}$	1.67 ± 0.67	1 ± 0.00	1 ± 0.00	1 ± 0.00
Ba	mg kg $^{-1}$	310.33 ± 0.67	16.33 ± 0.88	17.67 ± 0.88	90.33 ± 0.88
La	mg kg $^{-1}$	91 ± 2.65	5 ± 0.00	5 ± 0.00	5 ± 0.00
Ce	mg kg $^{-1}$	169 ± 1.53	0.33 ± 0.33	n.d.	2 ± 1.53
Nd	mg kg $^{-1}$	83.33 ± 0.67	8 ± 0.00	8 ± 0.00	8 ± 0.00
Tl	mg kg $^{-1}$	n.d.	n.d.	n.d.	n.d.
Pb	mg kg $^{-1}$	4 ± 0.58	n.d.	n.d.	19.33 ± 0.67
Th	mg kg $^{-1}$	16.33 ± 0.33	3 ± 0.00	3 ± 0.00	3 ± 0.00
U	mg kg $^{-1}$	4 ± 0.00	4 ± 0.00	4 ± 0.00	4 ± 0.00

n.d. - not detected, numbers after ± are standards errors of means (n = 3)

Serpentine and dunite also had relatively higher amounts of Mn, Cr, Co, and Ni (all ranging from ≤ 73 to 1177 mg kg $^{-1}$) compared to soda glass (ranging from 6.33 to 105 mg kg $^{-1}$). Soda glass, however, had higher Sr, Zr, Ba, and Pb contents than serpentine and dunite, but these concentrations were generally too low to be of any major concern in the final product (at ≤ 90.3 mg kg $^{-1}$). For example, applying about 30 kg of P ha^{-1} would result in a soil Pb concentration change of roughly < 0.6 ppm and given that the background concentration is < 50 ppm for arable cropping fields in Zimbabwe (Muchuweti *et al.*, 2006), the resulting Pb levels would be below general upper limits (Amoakwah *et al.*, 2020; Muchuweti *et al.*, 2006).

The contents of Si in serpentine and dunite were 53 and 55%, respectively, of the content in soda glass (33.58%). At a fixed mixing ratio by mass, soda glass will deliver twice the quantity of Si for the sintering reaction than serpentine and dunite. The Si content in serpentine and dunite used in this study is comparable to that of serpentine minerals analysed from the Mashava igneous complex in Zimbabwe, which had Si contents of up to 21.71%, with a slightly lower Fe content of 3.25% (Chaumba, 2019). Silicate minerals from the Mashava igneous complex can potentially provide a ready source of silicate for sintering the DPR, due to their proximity (100 km radius).

4.3.2 Mineral phases in raw materials

Mineral phase analysis revealed that the dunite sample consisted of lizardite, kellyite, and ferroan forsterite, while serpentine consisted of lizardite and chrysotile (Figure 4.1). The DPR consisted of mainly hydroxy-fluorapatite and calcite while soda glass was non-crystalline. The higher content of Mn in the dunite compared to serpentine is probably a result of the mineral kellyite $(Mn_{1.82}Al_{0.84}Mg_{0.24}Fe_{0.09})(SiO_{0.98}Al_{1.02}O_5)$, which was not present in the serpentine sample. The serpentine resources in Zimbabwe from Mashava

igneous complex can be potentially used in the local sintering process. Chaumba (2019) reported the mineral phases in this local resource to consist of lizardite, chrysotile, and antigorite. The presence of chrysotile in serpentine means that extra care needs to be taken when handling the material to avoid inhaling the fine dust, as it is a potential cause of lung scarring (asbestosis) and lung cancer.

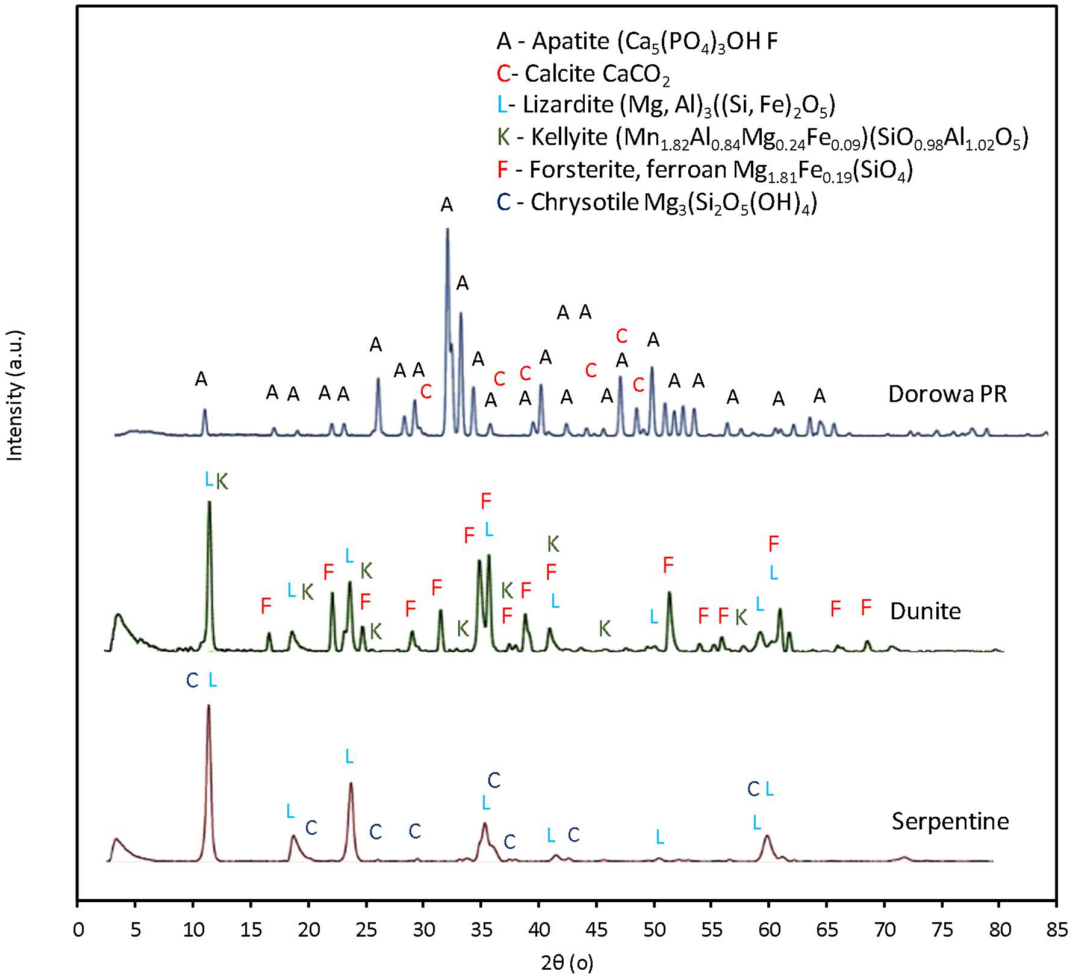

Figure 4.1 X-ray diffractograms of raw materials showing identified mineral phases (soda glass is not included because it was non-crystalline)

4.3.3 Thermal behaviour of straight and mixed materials

When thermally treated on their own to temperatures of up to 1200 ºC, DPR, soda glass, dunite and serpentine had total mass losses of 1.19, 0.86, 6.62 and 13.07%, respectively (Figure 4.2a).

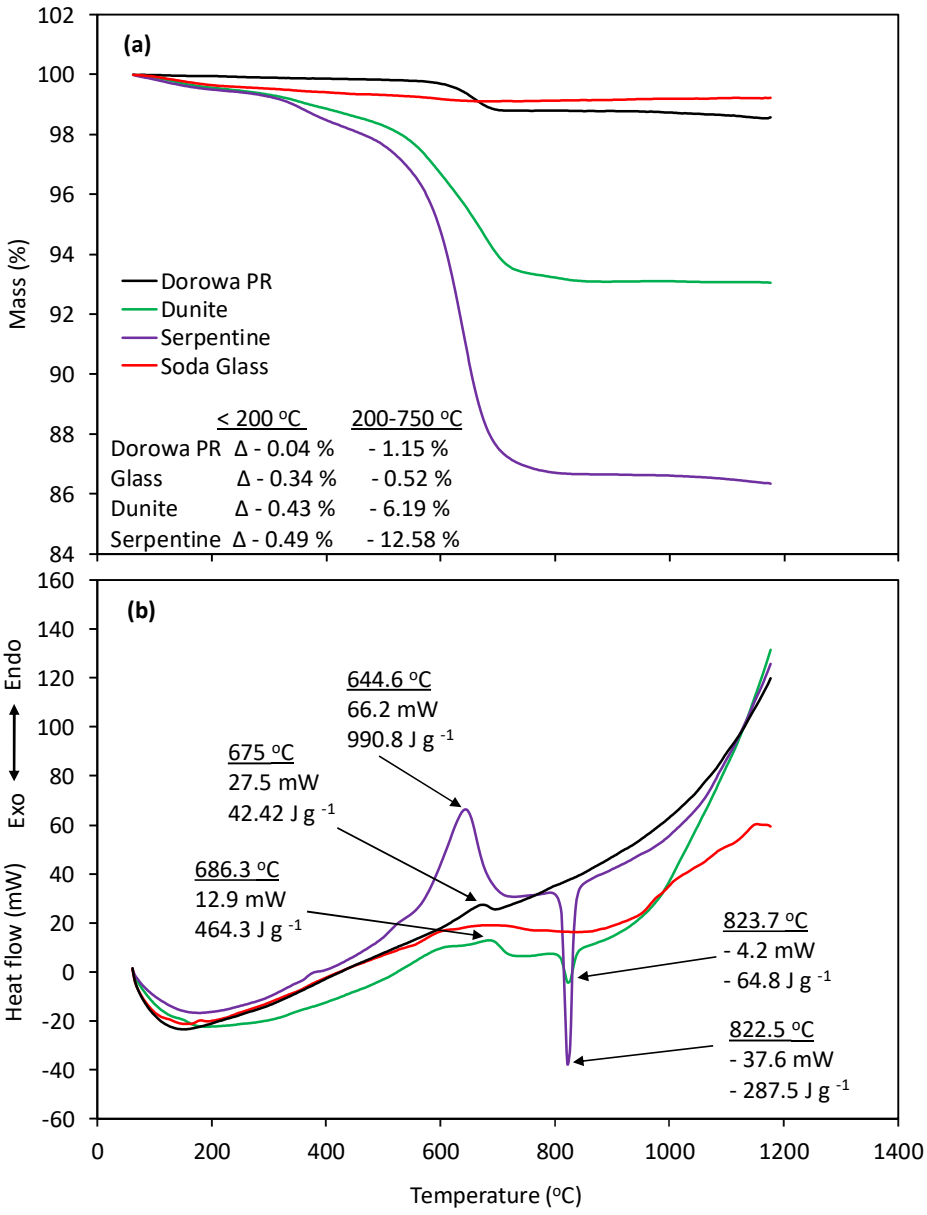

Figure 4.2 (a) Thermo-gravimetric analysis and **(b)** differential scanning calorimetry curves of DPR and the silicate additives used in the sintering process

The mass loss for soda glass was gradual, while DPR, dunite, and serpentine, had their highest mass change at temperatures that corresponded with DSC endothermic peaks at 675, 687, and 645 ºC, respectively. The mass loss at temperatures less than 200 ºC is a result of the removal of adsorbed water.

While the DSC signal for soda glass did not have any major peaks (Figure 4.2b), it started to plateau between 600 to 687 ºC, which indicated that the soda glass was absorbing energy and becoming more fluid. The endothermic DSC peaks for serpentine and dunite at 687 and 645 ºC, respectively, are the result of de-hydroxylation reactions (removal of structural hydroxyl groups as water) that disorder the mineral structure and form a more reactive dehydroxylate ($Mg_3Si_2O_7$). The endothermic peak temperatures observed are slightly lower than those indicated by Dlugogorski and Balucan (2014), who reported decomposition temperatures of lizardite and chrysotile to range from 708 to 714 ºC and from 650 to 654 ºC, respectively.

At around 823 ºC, both dunite and serpentine had exothermic DSC peaks that corresponded with re-crystallisation reactions. In particular, is the conversion of $Mg_3Si_2O_7$ (metachrysotile) to Mg_2SiO_4 (forsterite) according to equation 4.2 below (Raschman *et al.*, 2013):

$$2Mg_3Si_2O_{7(S)} \rightarrow 3Mg_2SiO_{4\,(s)} + SiO_{2\,(s)} \qquad \textbf{(4.2)}$$

Energy released during this process was 64.8 J g^{-1} for dunite and 287.5 J g^{-1} for serpentine suggesting that there was relatively less recrystallisation in dunite compared to serpentine. The dunite contains a significant amount of forsterite before calcination as observed from XRD analysis. Serpentine is dunite (or peridotite) that has been naturally heated by metamorphism and hydrothermally altered, so that the original olivine and pyroxene

minerals have been converted to serpentine. When serpentine is sintered, the hydrothermal alteration of dunite to serpentine that took place in nature is reversed.

When the DPR was mixed with soda glass, dunite and serpentine in various ratios, the thermal behaviour of each mixture was similar to that of the straight materials. Peaks were observed at the same temperatures as when the straight materials were calcined on their own (Figure 4.3).

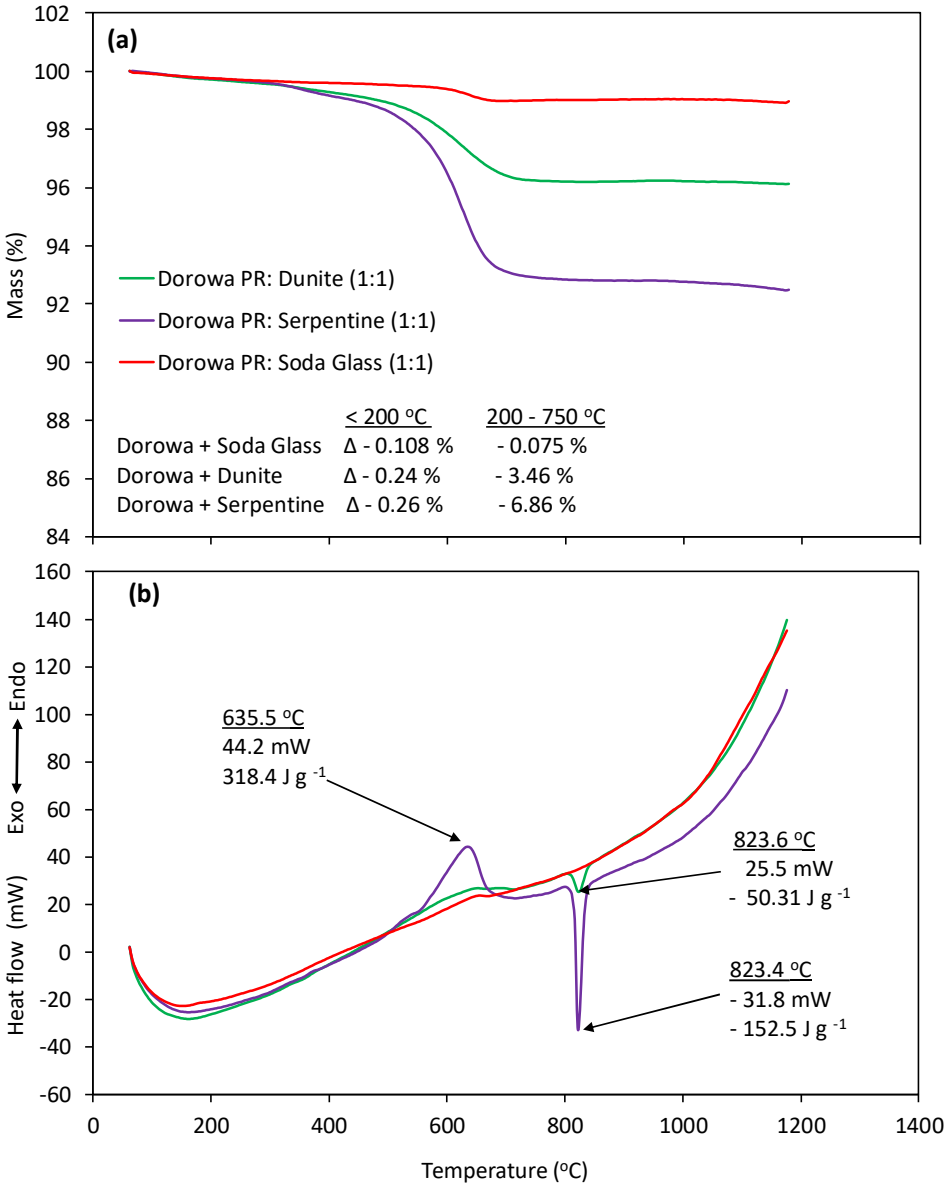

Figure 4.3 (a) TGA and **(b)** DSC curves of the DPR during sintering with soda glass, serpentine and dunite when mixed 1:1

Greater mass loss in sintered products when mixed with serpentine (since serpentine contains more hydration water) suggests that the final serpentine-mixed product will have a higher % P compared to dunite and soda glass. Sintering temperatures of 900 and 1000 ^{o}C were selected to allow de-hydroxylation and re-crystallisation reactions to take place based on the thermal behaviour of the mixed raw materials.

4.3.5 Mineral phases after sintering

Analysis of mineral phases in the final products indicated that all the lizardite, kellyite, and chrysotile originally present in dunite and serpentine were no longer present after sintering (Figure 4.4).

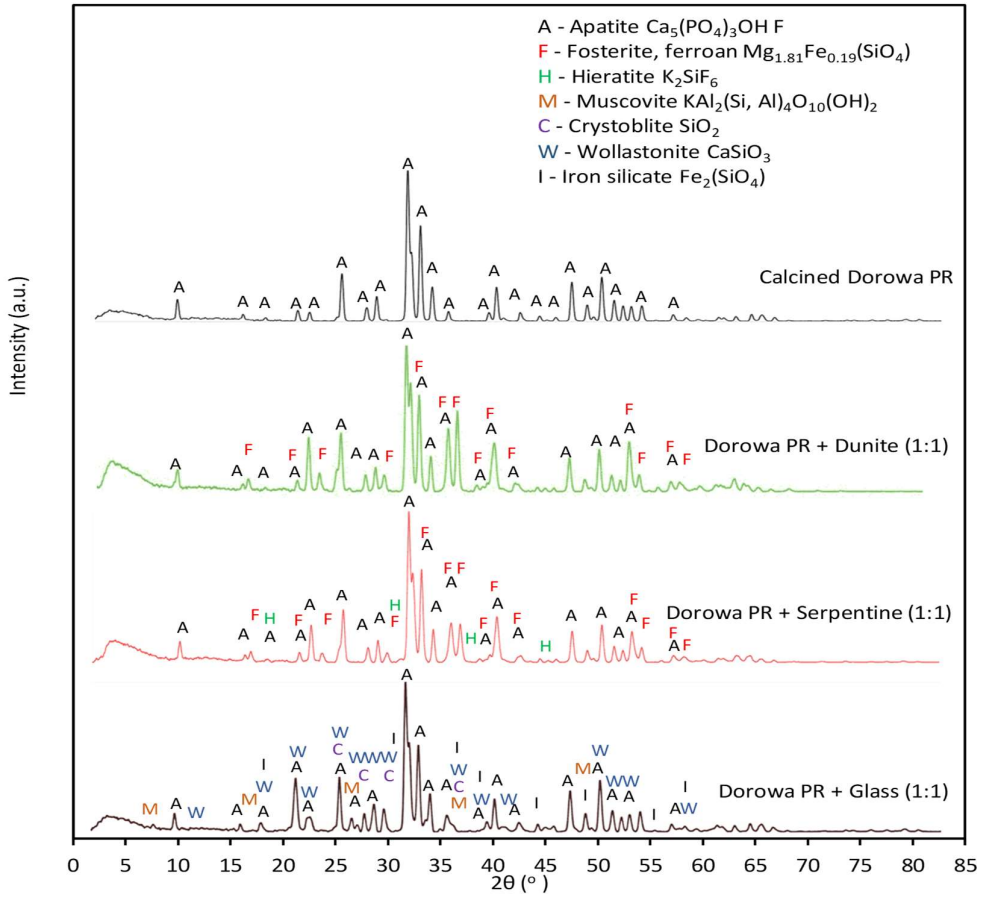

Figure 4.4 PXRD diffractograms of calcined and sintered products of DPR

Thermally mobilised silica (Equation 4.2) was likely incorporated into the PR's apatite structure in the serpentine and dunite mixtures, as evidenced by the observed lack of identification of quartz, or its polyforms, in these mixtures. Substitution of PO_4^{3-} by SiO_4^{4-} could not be detected using XRD techniques, suggesting the lack of structural changes in the apatite lattice of the sintered products. This is plausible, since Arcos *et al.* (2004) found that there was no significant P–O bond elongation in the apatite lattice after SiO_4^{4-} substituted for PO_4^{3-}, at a total Si content of 0.9%, in the final product.

When mixed with soda glass, iron silicate ($Fe_2(SiO_4)$), wollastonite ($CaSiO_3$), and quartz (SiO_2) polyforms were identified in the sintered product together with hydroxy-fluorapatite. Since Fe content was low in the original soda glass, we speculate that the Fe incorporated into iron silicate was predominantly sourced from the DPR. Some of the silica in the soda glass was converted to quartz as indicated by the appearance of this peak in the sintered product.

4.3.6 Solubility of P and selected elements in citric acid

Total P in the final products was either the same as, or more, than the total P of the pre-sintered mixed samples. Generally, samples sintered at 1000 ^oC had greater total P values compared with those that had the same mixing ratio and were sintered at 900 ^oC (Table 4.2). The greater mass loss during sintering of serpentine mixtures, noted in the "Thermal behaviour of raw and mixed materials" section, led to a more P-enriched final product compared to when other additives were used. The type of silicate additive, the amount added, and the sintering temperature, significantly ($P < 0.05$) affected the citric P solubility of the sintered samples. The amount of citric soluble P was generally in the order 1:2 > 1:1 > 2:1 for the DPR/ silicate mixtures. All the 1:2 mixtures, except the serpentine mixture sintered at 1000 ^oC, had greater than 36% citric soluble P at both

sintering temperatures. The 2:1 mixtures of serpentine and glass that were sintered at 900 ^{o}C presented approximately 65 and 4% more citric soluble P compared to their analogues at 1000 ^{o}C.

Table 4.2 Citric soluble P of sintered products

Mixture	Sintering Temp (^{o}C)	Air cooled		Water-quenched	
		Total P (%)	Citric Sol P (% of total P)	Total P (%)	Citric Sol P (% of total P)
33 % initial DPR content (LSD 2.295)					
DPR + Soda Glass	900	5.6 ± 0.001	39.1 ^{cd} ± 0.54	n.m.	n.m.
DPR + Serpentine	900	6.0 ± 0.016	41.5 ^{e} ± 0.74	n.m.	n.m.
DPR + Dunite	900	5.6 ± 0.016	36.7^{b} ± 0.10	n.m.	n.m.
DPR + Soda Glass	1000	5.5 ± 0.032	37.6^{bc} ± 0.35	n.m.	n.m.
DPR + Serpentine	1000	6.3 ± 0.040	25.1^{a} ± 0.16	n.m.	n.m.
DPR + Dunite	1000	6.1 ± 0.016	40.6^{de} ± 0.10	n.m.	n.m.
DPR + Sand (not heated)	-	5.5± 0.004	24.2^{a} ± 0.02	n.m.	n.m.
50 % initial DPR content (LSD 3.951)					
DPR + Soda Glass	900	8.5 ± 0.001	34.2^{d} ± 0.88	8.5 ± 0.002	32.6^{e} ± 0.73
DPR + Serpentine	900	9.0 ± 0.001	30.1^{c} ± 0.92	9.0 ± 0.11	28.7^{de} ± 0.02
DPR + Dunite	900	8.5 ± 0.001	28.6^{c} ± 0.61	8.8 ± 0.04	24.2^{bc} ± 0.42
DPR + Soda Glass	1000	8.6 ± 0.013	31.4^{cd} ± 0.52	8.4 ± 0.11	27.2^{cd} ± 0.63
DPR + Serpentine	1000	9.2 ± 0.194	21.1^{ab} ± 0.47	9.1 ± 0.001	22.9^{ab} ± 0.87
DPR + Dunite	1000	9.1 ± 0.001	23.7^{b} ± 0.25	8.9 ± 0.02	22.9^{ab} ± 0.98
DPR + Sand (not heated)	-	8.2± 0.01	19.7^{a} ± 0.06	8.2± 0.01	19.7^{a} ± 0.06
67 % initial DPR content (LSD 1.012)					
DPR + Soda Glass	900	11.5 ± 0.06	23.6^{d} ± 0.39	11.5 ± 0.09	25.9^{e} ± 0.29
DPR + Serpentine	900	11.8 ± 0.002	20.0^{c} ± 0.30	11.9 ± 0.08	23.6^{d} ± 0.75
DPR + Dunite	900	11.7 ± 0.029	19.1^{c} ± 0.11	11.5 ± 0.13	20.6^{c} ± 0.46
DPR + Soda Glass	1000	11.6 ± 0.078	27.6^{e} ± 0.27	11.5 ± 0.02	22.6^{d} ± 1.00
DPR + Serpentine	1000	12.1 ± 0.003	17.6^{b} ± 0.12	12.0 ± 0.10	17.9^{b} ± 0.92
DPR + Dunite	1000	11.8 ± 0.203	19.7 ^{c} ± 0.32	11.7 ± 0.02	19.8^{c} ± 1.46
DPR + Sand (not heated)	-	11.0± 0.005	16.3^{a} ± 0.01	11.0± 0.005	16.3^{a} ± 0.01
100 % DPR (LSD 1.109)					
DPR	900	17.1 ± 0.079	14.0^{b} ± 0.07	16.9 ± 0.01	14.1^{b} ± 0.47
DPR	1000	17.6 ± 0.003	14.1^{b} ± 0.01	17.1 ± 0.02	16.2^{c} ± 0.25
DPR (not heated)	-	16.5 ± 0.09	12.1^{a} ± 0.04	16.5 ± 0.09	12.1^{a} ± 0.04

n.m. - not measured, numbers after ± are standards errors of means (n=3), superscript letters indicate significant differences within a column for products with the same initial DPR content

The relative increase in citric acid soluble P of the final products was evaluated using a baseline control of the DPR mixed with acid-washed sand to evaluate the dilution effect associated with a widening in the P to citric acid ratio (Figure 4.5). Compared to the DPR/ sand baseline, there was a minimal increase (< 8%) in citric soluble P for all air-cooled serpentine mixtures that were sintered at 1000 ºC (Figure 4.5).

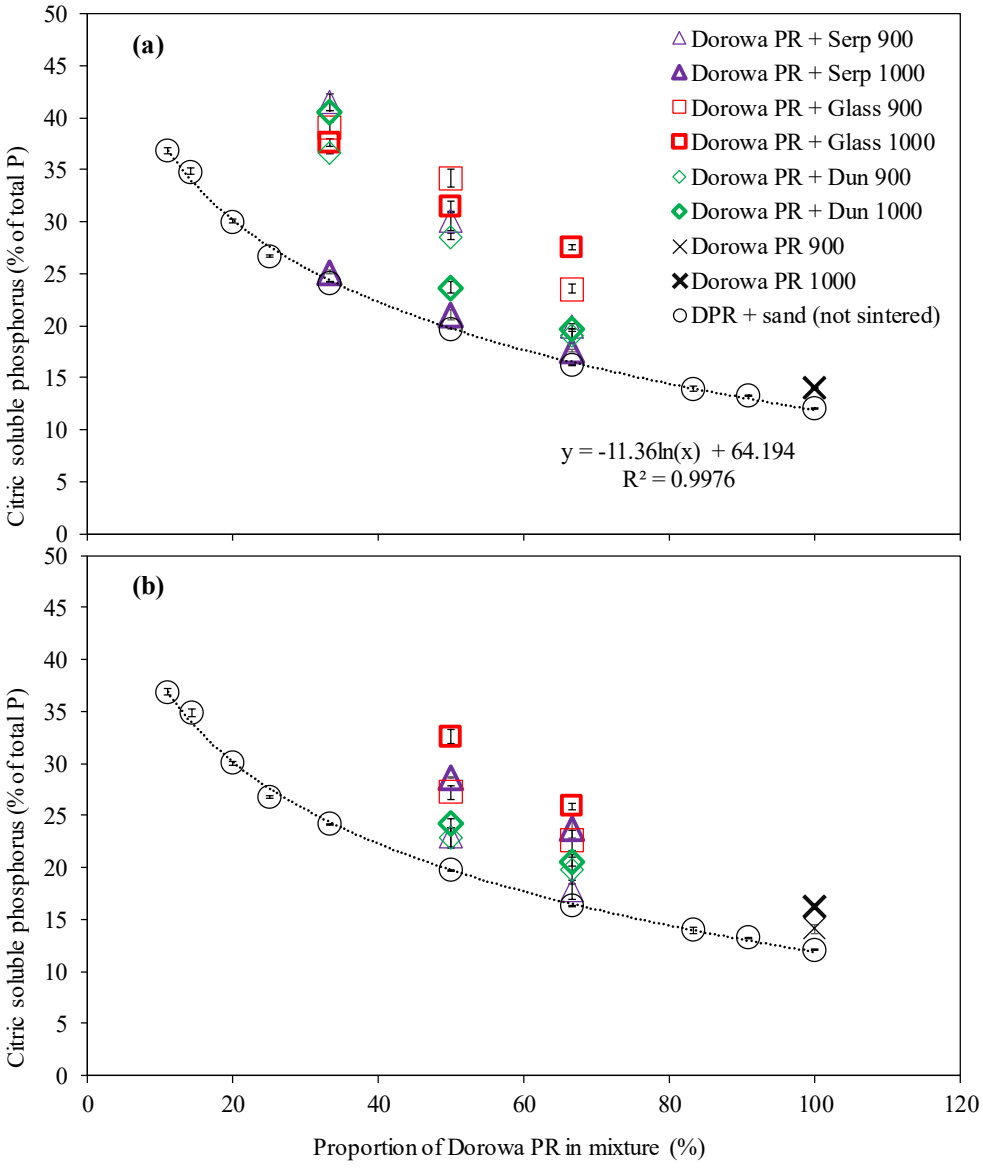

Figure 4.5 Comparison of citric soluble P of sintered products with unamended DPR, after the products are (a) air cooled and (b) water quenched. Error bars represent 2x standard error of means

The DPR/ soda glass mixtures that were sintered at 900 ºC and air-cooled, resulted in an increase of citric soluble P of 62, 73, and 44% from the baseline when mixed at 1:2, 1:1 and 2:1 ratios, respectively. For the serpentine analogues sintered at 900 ºC, citric soluble P increased by 72, 53, and 22% from the baseline at mixing ratios of 1:2, 1:1, and 2:1 (DPR/ additive), respectively.

Citric acid extractants from the products sintered at 900 ºC that exhibited high citric soluble P for the 1:1 and 1:2 mixes (DPR/ additive), were further analysed for dissolved Ca, Mg, Na, Fe and Al (Table 4.3) and compared to their raw mixtures (Appendix 1: Table S4.1). The unheated DPR had a relatively high amount of Ca that was solubilised by citric acid (49.7 mg g^{-1}, Appendix 1: Table S4.1). The likely sources are dissolution from the 1.4% of Ca which is present as $CaCO_3$ (Tumbure *et al.*, 2019) and some from Ca in the apatite. The incongruent dissolution of Ca:P is evident from the 1.9 Ca:P molar ratio of the citric acid extract (Appendix 1: Table S4.2) as compared to the 1.7 Ca:P molar ratio in the DPR. The sintered DPR and serpentine/dunite mixtures had an increase in citric soluble Ca of at least 43% compared to their raw mixtures, while for DPR and glass mixtures sintering increased citric soluble Ca by about 19 – 35% only (Table 4.3 and Appendix 1: Table S4.1). The increased Ca solubility can be explained by the removal of Ca from the apatite structure as a result of Mg^{2+}/Na^{+} substitution.

The DPR and serpentine/ dunite mixtures had a significant amount of Mg that was solubilised by citric acid (> 8 mg g^{-1}) representing an increase of between 39 to 141% from their raw mixtures and this could potentially be bio-available, adding to the Mg needs of a growing crop. The sintered DPR/ glass mixtures had increased soluble Na of at least 117% compared to their raw counterparts (Table 4.3 and Appendix 1: Table S4.1).

Table 4.3 Selected citric acid soluble elements from products sintered at 900 °C and air-cooled

Mixture	Initial DPR content (%)	Ca	Mg	Na	Fe	Al
		Citric acid soluble (mg g $^{-1}$)				
DPR + Soda Glass	33	42.7 ± 1.9	0.3 ± 0.03	6.4 ± 0.1	0.3 ± 0.01	0.2 ± 0.01
DPR + Soda Glass	50	45.7 ± 0.6	0.2 ± 0.002	5.0 ± 0.004	0.2 ± 0.01	0.2 ± 0.02
DPR + Serpentine	33	42.9 ± 0.5	11.6 ± 0.6	0.8 ± 0.02	1.9 ± 0.1	0.5 ± 0.01
DPR + Serpentine	50	55.7 ± 0.5	10.1 ± 0.02	0.7 ± 0.02	2.0 ± 0.02	0.7 ± 0.01
DPR + Dunite	33	41.4 ± 0.9	9.6 ± 0.1	1.1 ± 0.2	2.2 ± 0.04	0.8 ± 0.02
DPR + Dunite	50	52.4 ± 0.4	8.9 ± 0.04	0.8 ± 0.03	2.3 ± 0.02	1.2 ± 0.02
		Citric acid soluble (% of total content)				
DPR + Soda Glass	33	26	2	9	7	7
DPR + Soda Glass	50	21	2	9	4	7
DPR + Serpentine	33	35	7	52	5	13
DPR + Serpentine	50	30	8	34	7	20
DPR + Dunite	33	32	6	49	5	11
DPR + Dunite	50	27	7	32	6	21

numbers after ± are standard errors of means (n = 3)

The very low level of solubilised Fe and Al (< 0.3 mg g^{-1}) in DPR/ glass products mean that there are less chances of issues to do with formation of insoluble Fe/Al phosphates in soils where they may potentially be used. For example, Waclawska *et al.* (2011) reported that the formation of domains with phosphate-like structure and having chemically stable P-O-Fe^{3+} and P-O-Fe^{2+} bonds decreases the glass solubility under conditions simulating the soil environment. For the DPR/ dunite mixtures the relatively higher level of solubilised Fe (< 2.23 mg g^{-1}) could potentially limit the bioavailable P in the soil environment. The amount of citric acid soluble Fe in this study and for the mixtures with dunite was however only about 6% of the total Fe content in the dunite mixtures (Table 4.3). The sintered DPR/ glass mixture (33:67) is probably partially a phospho-silicate glass judging by the molar ratios of Ca, Mg, Na, Al and Fe with P of the citric acid dissolved elements which is similar to that reported by Barbieri *et al.* (2014) from animal flour glass fertiliser, which had similar high P solubility in 2% citric acid.

4.3.6 Practical Implications

Assuming the SSP fertiliser sold in southern Zimbabwe at a price of US $500 per tonne, contains an estimated 8.3% total P and about 80% of this is citric soluble, then the value of citric soluble P would be US $7.80 kg $^{-1}$. On a citric soluble P basis, unamended DPR with about 20 kg citric soluble P per tonne would have a relative value of US $158 per tonne. Whereas 900 ^{o}C sintered DPR/ glass products at 1:1 and 2:1 ratio containing about 29 kg and 27 kg citric soluble P per tonne, respectively, will have relative values of US $226 and US $211 per tonne, respectively. In-order to reduce costs, DPR would need to be sintered at the site of application because transport costs per unit of citric soluble P of the thermally altered product would be high.

4.4 Conclusions

Heating DPR with recycled glass resulted in chemical changes to the hydroxy-fluorapatite lattice through possible substitutions of PO_4^{3-} by SiO_4^{4-} and/or Mg^{2+}/Na^{+} for Ca^{2+} and Fe^{2+}. Thermal alteration led to improved citric solubility of up to 73% compared to the unamended DPR. Quenching was not necessary for improving the citric soluble P in the final DPR/ glass sintered products. Sintering at 900 ^{o}C in existing brick kilns is a potential low-cost alternative for improving the agronomic value of igneous the DPR. However, glasshouse and field tests to assess the 'true' agronomic value are recommended.

Results from experiments described in this chapter fully meet the thesis objective of investigating the effect of thermal alteration on P extractability of the DPR

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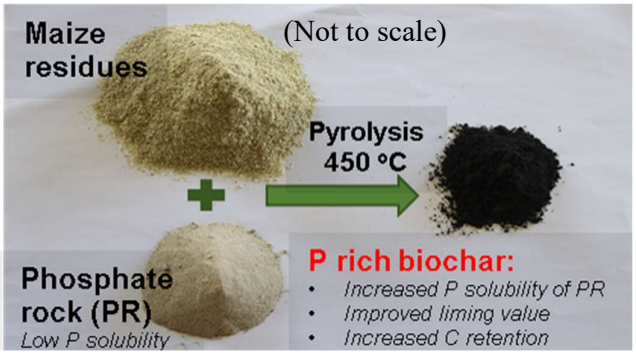
CHAPTER 5

CO-PYROLYSIS OF MAIZE STOVER AND IGNEOUS PHOSPHATE ROCK TO PRODUCE POTENTIAL BIOCHAR BASED P FERTILISER

Having numerous options for producing a phosphate rock (PR) product with improved agronomic value is essential to allow farmers to select the most practical option that fits well with their resource endowment, situation, or preference. This chapter discusses the production of a potential biochar-based P fertiliser using Dorowa PR and maize residues. This product could be a second option to using recycled glass previously discussed in Chapter 4. The rational is that some smallholder farmers who mainly grow maize but have few cattle herds could take advantage of co-pyrolysis to ameliorate their soil using residue biomass they already have.



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Abstract

A biochar product that can supply the phosphorus (P) needs of growing crops will be highly advantageous for smallholder farmers in acidic, P-fixing and P-deficient soils. In this study, nonreactive Dorowa phosphate rock (DPR) from Zimbabwe was added to maize residues (stems + leaves) at ratios of 1:2, 1:4, 1:6, and 1:8 (w/w) and pyrolysed at 450 ºC for 30 or 60 min to produce a suite of biochar-based fertilisers (BBFs). The total P, carbon (C), and nitrogen (N) retention, biochar yields, liming value, and the amount of citric-soluble P for these BBFs were assessed. After 60 min pyrolysis residence time, the 1:4, 1:6, and 1:8 mixtures yielded at least 26% more biochar yield, retained at least 43% more C and retained up to 26% more N in the biochar compared to the pyrolysis of maize residues only. Citric-soluble P of DPR increased up to 34 and 37% of total P in the BBFs produced from the 1:6 and 1:8 DPR + maize mixes. This translated to more than 30% increase in citric-soluble P compared to the unamended DPR. The BBFs show promising potential for supplying the P needs of growing crops, with about 2.1 tonne of the BBF (1:6 initial mix) being needed to supply 40 kg of citric-soluble P. The alkaline BBFs (pH > 10.2) had calcium carbonate equivalent values that ranged from 9.19 to 19.14 and are more suited for application to P-deficient, acidic soils. Glasshouse and field agronomic testing are recommended.

5.1 Introduction

The addition of biochar to soil is a potential strategy to retain carbon (C) in the soil (Whitehead *et al.*, 2018), and to condition the soil by reducing the toxicity of elements such as Pb and Cd in contaminated soils (Netherway *et al.*, 2019). There are several potential applications and benefits of adding biochar as a soil conditioner in sandy, acidic and low P soils (Huang *et al.*, 2017). Depending on feedstocks, biochar can reduce the effects of high soil acidity, and improve organic C and water retention of soils (Gwenzi *et al.*, 2017; Whitehead *et al.*, 2018; Li *et al.*, 2014; Zhao *et al.*, 2017). Despite these benefits, the use of biochar as a fertiliser is limited because it normally has very low levels of phosphorus (P) and nitrogen (N), with recent research based on nutrient enrichment before or after pyrolysis (Wang *et al.*, 2014; Xu *et al.*, 2016; Santos *et al.*, 2019; Huang *et al.*, 2017). The enrichment of biochar after pyrolysis takes advantage of its adsorbing properties to create slow-release fertilisers (Gwenzi *et al.*, 2017). While this method helps in minimising P fixing in weathered soils and P leaching losses, it does not address another major problem of the unavailability and unaffordability of soluble fertilisers reported by several researchers as being widespread in many developing country smallholder farming areas (Soropa *et al.*, 2018; Kafesu *et al.*, 2018).

Enriching biomass with other nutrient sources and then subjecting the mixed feedstock to pyrolysis is gaining interest as a potential way to develop improved biochar-based fertilisers (BBFs) (Huang *et al.*, 2017; Karim *et al.*, 2019; Zhao *et al.*, 2016). Phosphate compounds have been shown to improve C retention and oxidation stability in biochar by forming C-O-PO_3 and/or $(CO)_2PO_2$ complexes on biochar surfaces (Zhao *et al.*, 2014; Lustosa Filho *et al.*, 2017; Carneiro *et al.*, 2018; Gao *et al.*, 2019). Most of the available research focuses on the addition of water-soluble phosphates, such as phosphoric acid and

triple super phosphate to organic feedstock and as the study by Lustosa Filho *et al.* (2017) indicates, the final BBF can be acidic and unsuitable for acidic soils. Other addition sources such as MgO have been suggested to increase the pH (Lustosa Filho *et al.*, 2017; Carneiro *et al.*, 2018); however, the cost of producing such a fertiliser will quickly rise beyond the reach of many smallholder farmers who currently struggle to afford P-soluble fertilisers.

Published research is limited regarding the use of alternative low-cost P sources such as phosphate rocks (PRs) in co-pyrolysis processes and their effect on the P-supplying ability of the resultant BBF. Recently, Gao *et al.* (2019) reported that co-pyrolysing rape straw with PR consisting of fluorapatite and calcium magnesium carbonate improved the C retention and Pb removal properties of the biochar. The authors did not, however, report on the amount of P that became soluble in water or 2% citric acid. Smallholder farmers would benefit from a BBF that is cheap, can supply P and offers other benefits such as increasing soil water retention, soil organic C and correcting soil acidity problems. In southern Zimbabwe, smallholders have access to the local igneous Dorowa PR (DPR), but in its as-received state, it is unreactive with very low solubility value (Tumbure *et al.*, 2019). At the same time, maize residues which are the major crop residues widely available in Zimbabwe (Guyo *et al.*, 2015), are an ineffective organic nutrient source and are usually burnt by farmers without cattle. Combining the DPR and maize residues to produce biochar provides a more environmentally friendly option that can improve sustainable cropping in P-deficient soils.

This study tests the hypothesis that co-pyrolysis of maize stover with the igneous DPR from Zimbabwe will create a more soluble P source and liming material and lead to greater recovery of C in the BBF.

5.2 Materials and methods

5.2.1 Feedstock and additive preparation

The DPR was obtained from the Dorowa mine (19^0 03' 47" S, 31^0 45' 45" E) in Buhera, Zimbabwe. The DPR was previously characterised to have 16.5% total P, and 0.42% C existing as non water-soluble hydroxy-fluorapatite ($Ca_5(PO_4)_6OH$ F) and calcite ($CaCO_3$), respectively (Tumbure *et al.*, 2019). The DPR sample from the mine was already milled with approximately 94% of particles < 250 µm in diameter, and < 13% of the total P was soluble in 2% citric acid (Tumbure *et al.*, 2019). The rock was subsampled using a stainless steel riffler and finely ground to less than 150 µm using a RockLabs ring mill. The maize stover was used as the biochar feedstock because it is the major crop residue found in Zimbabwe because maize is grown as a staple crop (Kafesu *et al.*, 2018; Guyo *et al.*, 2015). Maize grown for silage was harvested on 4 March 2018, when it was still green from, Massey University, Hauronga Farm in Palmerston North when the crop had reached physiological maturity. The maize was separated into grain, cobs, husks and stems + leaves. The stems + leaves and cobs were separated and mechanically chipped using an electronic chipper before being dried to a constant mass in an oven at 70 ºC. All the biomass materials were then separately ground in a crosscutting mill to a particle size of < 2 mm.

5.2.2 Biochar production

The Maize stems + leaves (hereafter referred to as maize stover) and DPR were weighed into vitreous china crucibles with lids in the ratio 1:2, 1:4, 1:6, and 1:8 (DPR/ maize). All treatments were replicated 3 times, including a maize-only control. The total mass of the mixture in the crucibles was maintained at 4.5 g, and the crucibles were randomised on a

tray before they were placed into a muffle furnace. Hypoxic pyrolysis was performed by heating to 450 ^{o}C at a rate of approximately 16 ^{o}C/ min. A low-oxygen environment was achieved inside the crucibles during pyrolysis by the continuous emission of pyrolysis volatiles that prevented air from diffusing in through the lid (Lustosa Filho *et al.*, 2017; Gao *et al.*, 2018). After reaching the desired temperature, one set of samples were maintained at that temperature for 30 min and the other for 1 h.

5.2.3 Characterisation of feedstock and BBF materials

Mass changes and points of reaction were determined by running a thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis on a NETZSCH STA 449F1 Jupiter gravimetric thermal analyser. Samples consisted of DPR/maize that were thoroughly mixed together in the ratios 1:6 and 1:8 (DPR/ maize). Samples were placed in aluminium crucibles and heated up to 600 ^{o}C with a heating rate of 10 °C/ min. A protective N_2 gas flow of 20 mL/min and a purge N_2 gas flow of 50 mL/min was employed. Three separately mixed feedstock material for each treatment were individually analysed to check if the mixing had been homogenous.

BBFs were ground in a tungsten carbide ring grinder before analysis. Carbon, H, and N content, both in the biomass feedstock and the produced biochar, was determined using an Elementar analyser (Elementar, Vario MACRO, Germany). The total biochar yield was calculated in order to evaluate the relationship between the quantity of feedstock used and the amount of the final BFF produced. While the total biochar yield is important for fertiliser calculations, the proximate biochar yield that subtracts the contribution of the mineral additive was also calculated to assess if there was an overall catalytic increase in biomass losses during pyrolysis. The C sequestrating value of biochars was inferred from C retention and aromaticity of biochars. The total biochar yield, proximate yield, and C

and N retention of biochar were calculated according to equations (5.1), (5.2), (5.3), and (5.4) respectively, as follows (Carneiro *et al.*, 2018; Zhao *et al.*, 2017);

$$\text{Total Biochar Yield \%} = \left(\frac{W_{bioch}}{W_{biomass} + W_{additive}} \right) \times 100 \qquad (\mathbf{5.1})$$

$$\text{Proximate Yield \%} = \left(\frac{W_{biochar} - W_{additive}}{W_{biomass}} \right) \times 100 \qquad (\mathbf{5.2})$$

$$\text{C retention \%} = \frac{\text{C}_{\text{biochar}} \times \text{W}_{\text{biochar}}}{(\text{C}_{\text{biomass}} \times \text{W}_{\text{biomass}}) + (\text{C}_{\text{additive}} \times \text{W}_{\text{additive}})} \qquad (\mathbf{5.3})$$

$$\text{N retention \%} = \frac{\text{N}_{\text{biochar}} \times \text{W}_{\text{biochar}}}{(\text{N}_{\text{biomass}} \times \text{W}_{\text{biomass}}) + (\text{N}_{\text{additive}} \times \text{W}_{\text{additive}})} \qquad (\mathbf{5.4})$$

where C is the carbon content, N is the nitrogen content, and W is the mass. The subscripts represent the type of material. Prior to the total P analyses, feedstock materials and biochar were digested in a ternary acid mixture (1:1:1.4) of concentrated HCl (36%), HNO_3 (70%), and $HClO_4$ (70%). Diluted digests were then analysed for total P by UV-Vis spectrophotometry using a phospho-vanado-molybdate finish on a Jenway UV-Vis spectrophotometer (Hedley *et al.*, 1988; Fertmark, 2016). The resulting P reactivity of the BBFs were evaluated by extractions in 2% citric acid, which is an internationally recognised standard method for evaluating the fertiliser agronomic efficiency potential (EU, 2003; Fertmark, 2016; IFA, 2013). The citric-soluble P was measured using the same spectrophotometric method used for the total P after extraction in 2% citric acid on a shaker for 30 min (Fertmark, 2016). Previous studies have noted that when evaluating the reactivity of PRs using extractants such as 2% citric acid, the solid/solvent and

P/solvent ratios affect the fraction of P solubilised (Camps-Arbestain *et al.*, 2017). Inorder to control the effect of differing PR/solvent ratios, DPR + inert sand mixtures at various ratios were extracted in citric acid to allow comparisons between the BFF products and the original DPR at the same PR/solvent ratio. Interpretations on the suitability of the BBFs to acidic soils was done through measuring the pH and calcium carbonate equivalence (CCE) of the biochars. Biochar pH was measured using a Thermo Scientific Orion Star® A214 pH meter, after 24 h equilibration in a 1:10 (w/v) suspension of biochar and de-ionised water (Santos *et al.*, 2019; Ren *et al.*, 2019). The CCE of biochars were analysed by the back-titration method of Singh *et al.* (2017).

Chemical and structural changes in the BBF products were assessed by the analysis of crystalline phases conducted using the powder X-ray diffraction analysis. This was carried out on a Rigaku Spider X-ray diffractometer with Cu Kα radiation (the Rigaku MM007 microfocus rotating-anode generator), monochromated and focused with high-flux Osmic multilayer mirror optics, and a curved image plate detector. The ground DPR was fixed to a mount with a minimum amount of Fomblin oil. The sample diffraction pattern was imported and analysed by running Sleve+ software referencing the International Centre for Diffraction Data (ICDD), PDF-2 2019 database. The analysis of functional groups in the biochars was performed by Fourier-transform infrared (FTIR) spectroscopy using a Thermo Scientific Nicolet iS5 spectrometer. This allowed the qualitative identification of any changes in the biochar products caused by the addition of DPR. The FTIR spectra of ground samples were collected over an average of 32 scans with a resolution of 4 cm^{-1} and a range of 4000 to 400 cm^{-1}.

5.2.4 Statistical analysis

The variance in the citric acid-soluble P data was analysed with a two-way model to test the interactive effect of mixing ratios and pyrolysis residence time using R statistical software (version3.5.0). Significantly different means ($P < 0.05$) were separated by employing least significant differences. The assumptions of normality and equal variance were assessed by plotting normal QQ plots.

5.3 Results and discussion

5.3.1 Feedstock characterisation

Maize stems + leaves constituted about 42% of the total above-ground maize biomass on a dry weight basis, which is comparable to the grain at 41% (Table 5.1). Stems + leaves, because of their high biomass and lower economic value, were selected for co-pyrolysis experiments. In smallholder farming areas, maize residues have various uses that include bedding material in cattle pens, supplementary cattle feed, and as a mulch to cover the soil. It is a common practice for Zimbabwean smallholder farmers without cattle, to burn maize residues because they are an insufficient N source for crop production. Maize residues fall into the low-quality organic resource class for residues with <2.5% N, >15% lignin, >4% polyphenols, and >30 C/N ratio (Mtangadura *et al.*, 2017). The current maize stover (stems and leaves) used in this experiment had a C/N ratio of 40. When incorporated into the soil, there might be a temporary soil N "lock up" resulting from the high C/N ratio that encourages the immobilisation of soil N during microbial growth on the C-rich stover (Masvaya *et al.*, 2017). Once the grain is removed, maize cobs can be used as a fuel source.

Table 5.1 Selected elemental content and biomass partitioning in harvested maize

Plant part	% weight	P (%) w/w	N (%) w/w	C (%) w/w	H (%) w/w	S (%) w/w
Stems & leaves	42.1	0.22 ± 0.01	1.51 ± 0.09	60.44 ± 1.61	17.36 ± 0.44	0.51 ± 0.19
Grain	40.8	0.32 ± 0.01	2.22 ± 0.03	57.58 ± 1.30	19.34 ± 0.39	0.03 ± 0.002
Husks	6.6	0.08 ± 0.002	0.82 ± 0.04	61.05 ± 0.93	16.11 ± 0.27	0.03 ± 0.02
Cobs	10.5	0.04 ± 0.01	0.69 ± 0.08	49.15 ± 1.52	14.52 ± 0.66	0.05 ± 0.04

Numbers after ± are standard error of means, n = 3.

5.3.2 Pyrolysis and mass loss

Thermogravimetric (TG) and DSC analysis revealed that the pyrolytic process of both maize and DPR + maize consisted of 4 major stages that corresponded with 4 endothermic DSC peaks (Figure 5.1).

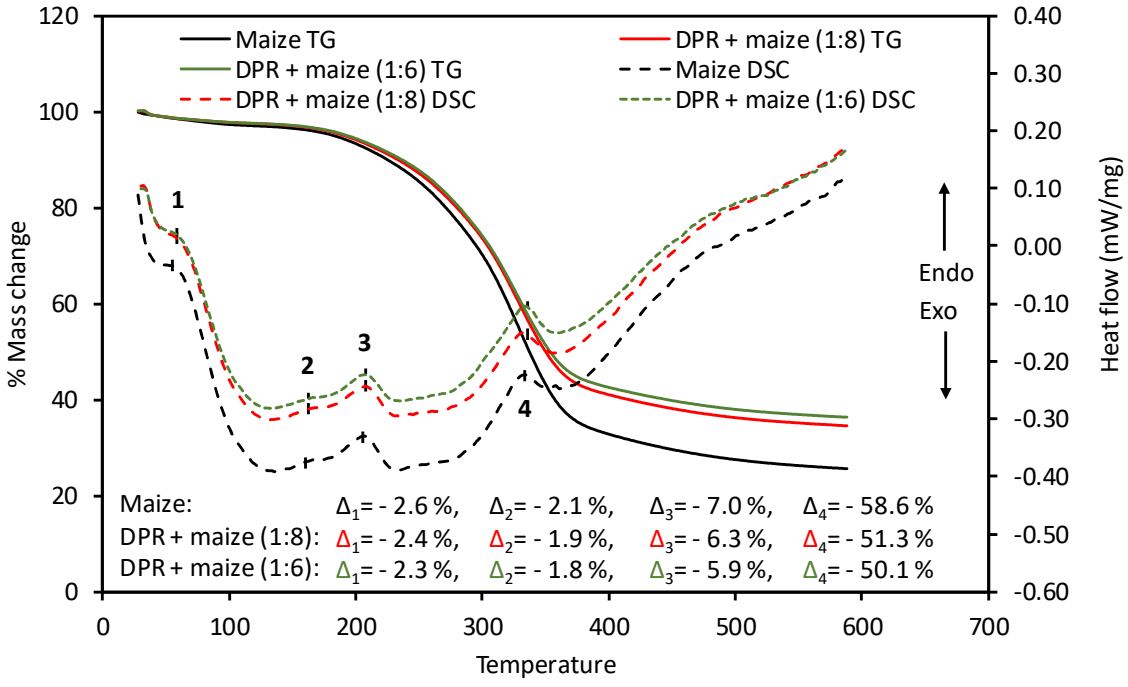

Figure 5.1 Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves of maize and DPR + maize mixtures during pyrolysis

The first stage, between 25 ºC to 120 ºC, was attributed to dehydration of non-structural water. The second and third stages, with endothermic peaks at 160 ºC and 205 ºC, are the result of bonds breaking down. The greatest mass loss during the pyrolytic process corresponded with an endothermic peak at around 333 ºC, attributing to the production of volatiles and carbonisation reactions.

At around 400 ºC, the maize had reduced to 33% of its original mass and the combined DPR + maize mixtures had reduced to 41 and 43% of their original mass when mixed at 1:8 and 1:6 (DPR/ maize), respectively. The % mass losses between 60-70% upon pyrolysis is similar to that reported by Gao et al. (2019) for rape straw and rape straw + PR biochar. When compared to the maize-only sample, the addition of the DPR led to a reduced overall mass loss during pyrolysis likely as a result of the added DPR that was added to the ash fraction of the biochar. Previous studies on the thermal stability of the DPR showed that when heated in air up to 500 ^{0}C, the DPR losses only 0.17% of its mass (Tumbure *et al.*, 2019). Additionally, the presence of the DPR is likely to have slowed down carbonisation reactions. Compared to the maize-only DSC curve, there was an overall endothermic shift in the DSC curves when the DPR was added (Figure 5.1) indicating that the DPR + maize mixtures were absorbing more energy at each reaction point than the maize-only sample. The upward endothermic shift probably resulted from the DPR particles occluding the maize stover particles from degradation as suggested by previous researchers (Gao *et al.*, 2018).

5.3.3 Total biochar yields and proximate yields

The addition of DPR to maize increased the total biochar yield in proportion to the amount of the DPR added, regardless of the residence time (Figure 5.2a). As seen in the TGA analysis, the DPR added more to the ash content in the final biochar.

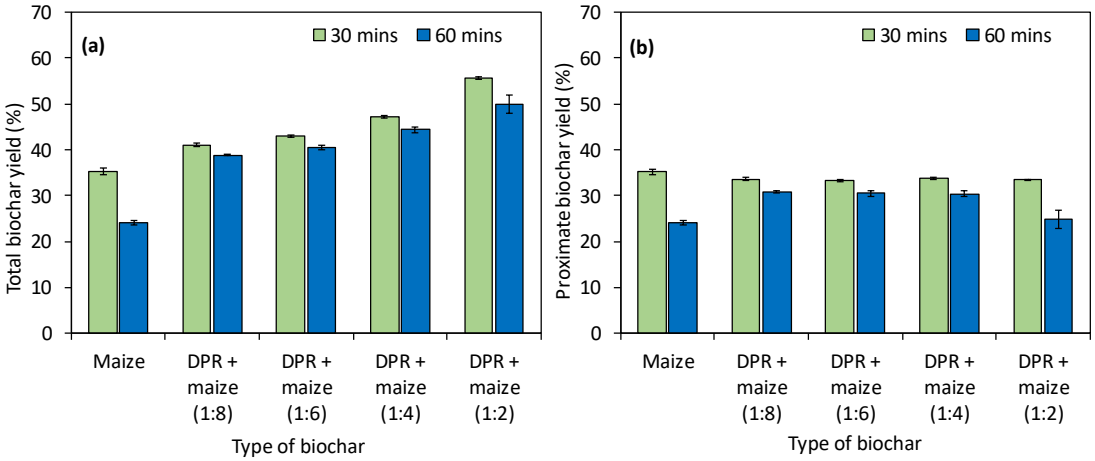

Figure 5.2 (a) Total biochar yield, and **(b)** proximate yield, after pyrolysis with or without DPR in various ratios. Error bars represent 2x standard error of means, n = 3

Compared to maize biochar, the total biochar yields increased by 58 and 108% when the residence time was 30 and 60 min respectively, at a 1:2 (DPR/ maize) premix ratio. It can be inferred that the residence time of 30 min was insufficient for the carbonisation of the material. Li *et al.* (2014) reported a similar trend of an increased total biochar yields when $Ca(H_2PO_4)_2$ was added to rice straws before pyrolysis.

The Proximate biochar yields revealed that at 30 min residence time, the addition of DPR prior to pyrolysis led to slightly increased losses in the proximate yield of up to 5.1% compared to the maize biochar (Figure 5.2b). However, at 60 min residence time, the DPR + maize biochars that were mixed at 1:8, 1:6, and 1:4 yielded at least 26% more proximate biochar yield from the biomass compared to the maize biochar. It is evident that at 30 min residence time, P and biomass reaction effects had not yet been significant to alter the pyrolysis reaction conditions in favor of increased proximate yields. The addition of phosphoric acid to saw dust prior to pyrolysis has also been reported to improve proximate yields (Zhao *et al.*, 2016).

5.3.4 Mineral phases and surface functional groups in co-pyrolysis products

Although all the diffraction peaks of identified minerals were matched with sample experimental data, only the 3 highest intensity peaks per identified mineral phase are discussed. High-intensity diffraction peaks at d-spacing of about 2.81, 2.78, and 2.71 in the DPR and co-pyrolysis biochars were identified as hydroxyl-fluorapatite $Ca_5(PO_4)_3(OH)F$ (Figure 5.3). The diffraction peaks at d-spacing of about 3.04, 2.28, and 2.10 were identified as calcite ($CaCO_3$). Hydroxy-fluorapatite and calcite that were present in the co-pyrolysed biochars were originally from the DPR. The presence of sylvite (KCl) in all the biochars was confirmed by diffraction peaks at d-spacing of about 3.52, 2.22, and 1.82. Other studies have reported sylvite in the P-added biochar (Ren *et al.*, 2019; Gao *et al.*, 2018). Crystalline C was also identified in the biochars that was not present in the DPR.

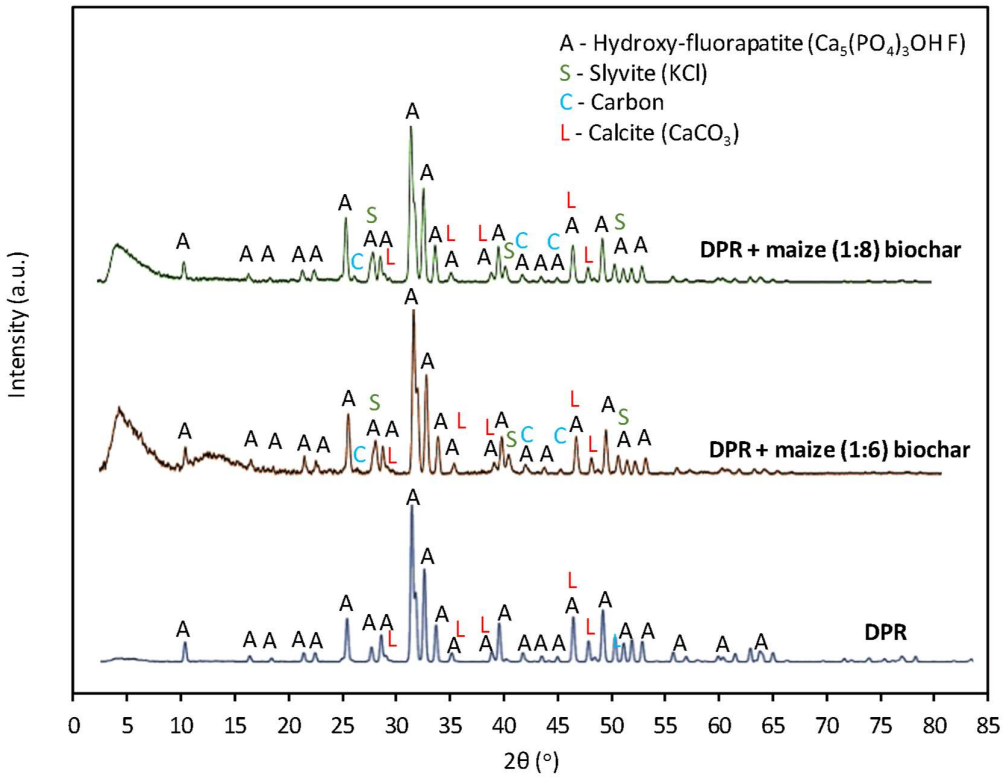

Figure 5.3 X-ray diffractograms of the co-pyrolysed DPR + maize biochars and the major mineral phases

The FTIR spectra of the maize stover revealed a broad peak in the region 3000 - 3667 cm^{-1} (Figure 4), which indicated stretching vibrations of hydroxyl groups from carboxyls, phenols, or alcohols, and water (Carneiro *et al.*, 2018; Lustosa Filho *et al.*, 2017; Pereira *et al.*, 2015). Peaks around 2920 and 1738 cm^{-1} were attributed to symmetric C−H stretching vibrations in aliphatics (Carneiro *et al.*, 2018; Lustosa Filho *et al.*, 2017) and carbonyl C=O (Guyo *et al.*, 2015) respectively. All the aforementioned peaks were absent in the biochar products because of the dehydration and decomposition/conversion reactions during pyrolysis.

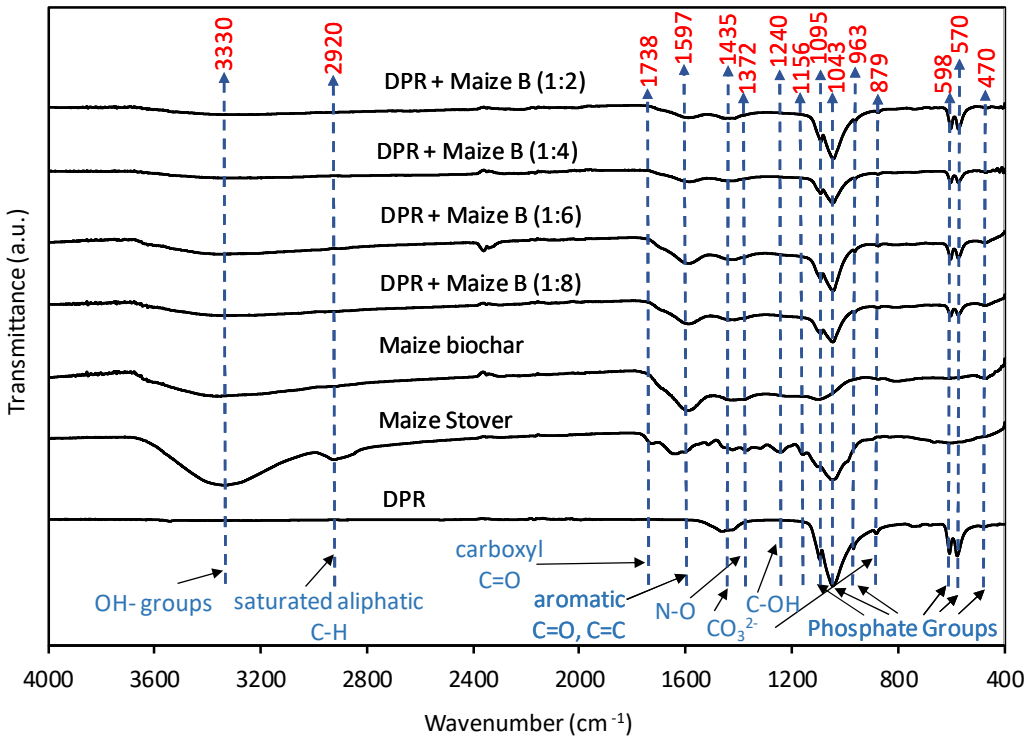

Figure 5.4 FTIR spectra of feedstock and their resultant biochars when pyrolysed at 60 min residence time.

A peak in the maize stover around 1372 attributed to N-O bonds was also observed (Guyo *et al.*, 2015). All the biochars were characterised by a shoulder at around 1597 cm^{-1} attributable to C=O and C=C stretching of aromatic rings (Zhao *et al.*, 2016; Gao *et al.*,

2018; Pereira *et al.*, 2015). Increasing amounts of DPR in the biochar caused a reduction in the relative intensity of the signal in this area, suggesting a reduction in aromaticity. This is likely because of two reasons; first, there was less contribution of maize to the biochar as the DPR content increased, and second, the effect of the DPR in slowing down the carbonisation rates as noted by some authors (Gao *et al.*, 2018).

A shoulder around 1435 cm^{-1} in the DPR and all biochars was attributed to both carbonates (CO_3^{2-}) (for DPR exclusively) and C=C and/or saturated C−H bending vibrations (Carneiro *et al.*, 2018; Zhao *et al.*, 2016). Carbonate in the DPR and co-pyrolysis biochars was further confirmed by a peak at 879 cm^{-1} (Tatzber *et al.*, 2006; Calle-Castaneda *et al.*, 2017), which supported XRD analysis data. Co-pyrolysis biochars and the DPR had a peak around 1095 that was attributed to the symmetric phosphate (PO_2^-) stretching, the P−O−C stretching, and the symmetrical P−O−P vibration in polyphosphate chains (Carneiro *et al.*, 2018; Zhao *et al.*, 2016; Calle-Castaneda *et al.*, 2017). Co-pyrolysis biochars, the DPR and the maize stover had a peak around 1043 that is characteristic of P-O-P stretching (Gao *et al.*, 2018; Carneiro *et al.*, 2018). In the maize stover, this peak probably resulted from P-containing organic esters which were degraded during pyrolysis because the peak was absent in the maize biochar. Peaks around 963, 598, and 570 cm^{-1} are attributed to the phosphate groups (PO_4^{3-}) in the apatite lattice of DPR (Calle-Castaneda *et al.*, 2017), whose relative intensities in co-pyrolysis biochars increased with increase in the DPR added. The peaks were absent in the maize stover and maize biochar.

5.3.5 Selected chemical properties of biochars

All the biochars produced were highly alkaline with pH ranging from pH 10.2 to 10.9 (Table 5.2). The biochars produced with a residence time of 60 min were slightly more

alkaline (pH 10.7 – 10.9) than those produced at 30 min residence time (pH 10.2 – 10.5). The DPR in water maintains a lower pH of 9.6, indicating more rapid liming ability of the biochars. Gao *et al.* (2018) reports a similar pH range for the rape straw biochar and co-pyrolysis biochars of rape straw + Chinese PR. Contrary to BFFs produced from water-soluble P compounds that are acidic (pH 2 to pH 5), premixing with the igneous PR produces an alkaline biochar that would be ideal for use especially in acidic soils.

Table 5.2 Selected chemical characteristics of produced biochars.

biochar	pH	P % (w/w)	N % (w/w)	C % (w/w)	H % (w/w)	H/C	CCE (%)
30 mins residence time							
maize	10.2 ± 0.04	0.3 ± 0.01	2.08 ± 0.23	63.72 ± 2.71	2.89 ± 0.55	0.61	7.84
DPR + maize (1:8)	10.3 ± 0.09	4.4 ± 0.07	1.28 ± 0.01	46.26 ± 0.17	2.94 ± 0.08	0.76	9.19
DPR + maize (1:6)	10.5 ± 0.08	5.4 ± 0.04	1.22 ± 0.03	43.50 ± 1.18	2.78 ± 0.09	0.77	10.63
DPR + maize (1:4)	10.4 ± 0.08	6.9 ± 0.04	1.06 ± 0.04	38.83 ± 1.93	2.37 ± 0.08	0.73	12.31
DPR + maize (1:2)	10.2 ± 0.09	9.8 ± 0.06	0.87 ± 0.07	30.01 ± 3.62	1.78 ± 0.26	0.71	18.95
60 mins residence time							
maize	n.d.	0.3 ± 0.01	1.93 ± 0.05	56.41 ± 0.98	3.02 ± 0.10	0.64	9.40
DPR + maize (1:8)	10.8 ± 0.01	4.6 ± 0.05	1.35 ± 0.02	45.44 ± 0.21	2.48 ± 0.04	0.66	11.54
DPR + maize (1:6)	10.9 ± 0.06	5.6 ± 0.08	1.17 ± 0.01	42.10 ± 0.60	2.21 ± 0.05	0.63	12.05
DPR + maize (1:4)	10.7 ± 0.06	7.4 ± 0.04	1.01 ± 0.02	35.09 ± 0.43	1.83 ± 0.06	0.63	14.36
DPR + maize (1:2)	10.8 ±0.06	11.0 ± 0.39	0.68 ± 0.02	20.84 ± 2.22	1.06 ± 0.12	0.61	19.14

Numbers after ± denote standard errors of means (S.E.M.), n =3, n.d. not determined

CCE of the biochars were in the order 60 min > 30 min residence time and increased with greater addition of the DPR in the pre-mix. The unamended DPR had a CCE of 34.6% (data not shown), while co-pyrolysis biochars ranged 9.19 to 19.14%. The PRs are known to provide liming action through the dissolution of PO_4^{3-}, CO_3^{2-}, and F^- from apatite minerals and CO_3^{2-} from carbonate gangue minerals (Loganathan *et al.*, 2005). The poorly

soluble igneous PRs, however, do not exhibit their liming potential in the soil environment (Sikora, 2002). The biochar liming potential is usually well correlated to the ash fraction, and the effects of chemical composition of the ash fraction can also be significant (Singh *et al.*, 2017).

The total P content of the resultant biochar was comparable (within 0.3%) to the estimated values calculated with the assumption that there were no P losses during the pyrolytic process. Increasing the residence time from 20 to 60 min resulted in a minimal increase in the total P content of the biochar (Table 5.2). At 30 min pyrolysis residence time, the maize biochar had an H/C ratio of 0.61 and the co-pyrolysis biochars had H/C ratios that ranged from 0.71 to 0.77, further confirming the reduced aromaticity in co-pyrolysed biochar noted in FTIR analysis. At 60 min residence time there was little difference between H/C ratios of co-pyrolysis and maize biochars indicating that for these treatments, carbonisation was more complete than at 30 min. The H/C ratios for maize biochar (0.61 and 0.64 at 30 and 60 min residence time, respectively) are comparable to those reported by Li *et al.* (2014) of 0.65 when the rice straw was pyrolysed in an N_2 gas atmosphere in a lab-scale pyrolysis reactor.

The DPR that was used in co-pyrolysis contains about 0.42% C present as carbonate, 16.5 % P present as hydroxy-fluorapatite, and does not contain any N (Tumbure *et al.*, 2019). DPR + maize biochars, therefore, had lower C and N content. Carbon retention of the maize biochar was similar to that of the DPR+ maize biochars at 30 min residence time (Figure 5.5a).

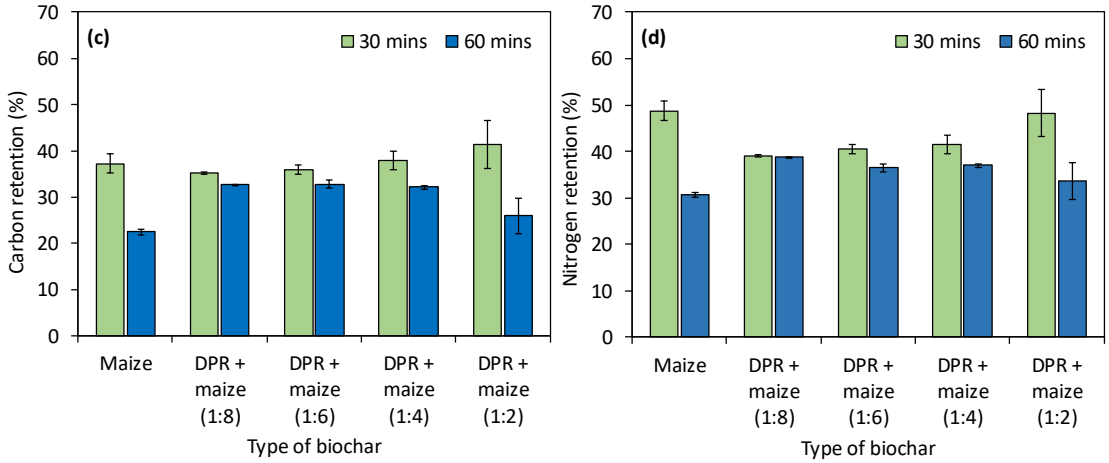

Figure 5.5 (a) Carbon retention, and **(b)** nitrogen retention of biochars after pyrolysis with or without DPR in various ratios. Error bars represent 2x standard error of means, n = 3

However, at 60 min residence time, and apart from the 1:2 mixture, the DPR + maize biochars had, at least, a 43% increase in C retention compared to the maize biochar. Other researchers have reported an increase in C retention of up to 27.5, 46.5, and 29% in biochars when PR, phosphoric acid, and $Ca(H_2PO_4)_2$, respectively, were added to biomass prior to pyrolysis (Carneiro *et al.*, 2018; Zhao *et al.*, 2017; Li *et al.*, 2014). The increase in C retention of co-pyrolysed biochar is due to reduced rates of carbonisation (Gao *et al.*, 2018). Carbon retention was comparable among the 1:8, 1:6, and 1:4 DPR + maize co-pyrolysed biochars. Increased C retention improves the potential of the BBF for sequestrating C in soils. However, the recalcitrant nature of the retained C should be further evaluated. The addition of DPR led to an initial increased N loss when the residence time was 30 min (Figure 5.5b). The DPR + maize biochars at 1:8, 1:6, 1:4 and 1:2 (DPR/ maize) mixing ratios had about 19.7, 16.8, 14.8, and 0.8% less N retained in the biochar respectively, compared to the maize biochar. However, when 60 min residence time was employed, the DPR + maize biochars eventually retained more N of up to 26% compared to the maize-only biochar. This shows that DPR addition can

minimise biomass N conversion to N_2 and/or NO_x - precursors and retain N in biochar. When applied to soil, retained N can potentially be taken up by the plant.

5.3.6 P solubility of biochars

All co-pyrolysis products were not soluble in water (soluble P < 0.02 % w/w). However, when extracted in 2% citric acid, there was a significant ($P < 0.01$) interactive effect between the level of the DPR added prior to pyrolysis and the residence time employed. DPR + maize biochars with mixing ratios of 1:6 and 1:8 (DPR/ maize) had up to 34 and 37% citric-soluble P respectively, regardless of the residence time. Considering the maize biochar which had a total P content of 0.3%, and 82% of this was citric acid soluble, the contribution of the maize stover toward citric-soluble P of all the co-pyrolysis biochars produced would be less than 6% of the total P. This confirms that the change in citric acid solubility was brought about mainly by the biomass + DPR reactions during pyrolysis. The assumption that there were insignificant P losses in the pyrolytic process, as confirmed by the total P results (Table 5.2), allowed us to estimate the final proportion of the DPR in the produced biochars. From these estimates, the DPR + maize biochars that were premixed at ratios of 1:2, 1:4, 1:6, and 1:8 (DPR/ maize) were calculated to end up with about 27.1, 33.3, 42, and 60% DPR in the final product, respectively. The citric solubility values of the biochars were compared to a baseline of unmodified DPR + sand, added as an inert material to give various acid to PR ratios (Figure 5.6).

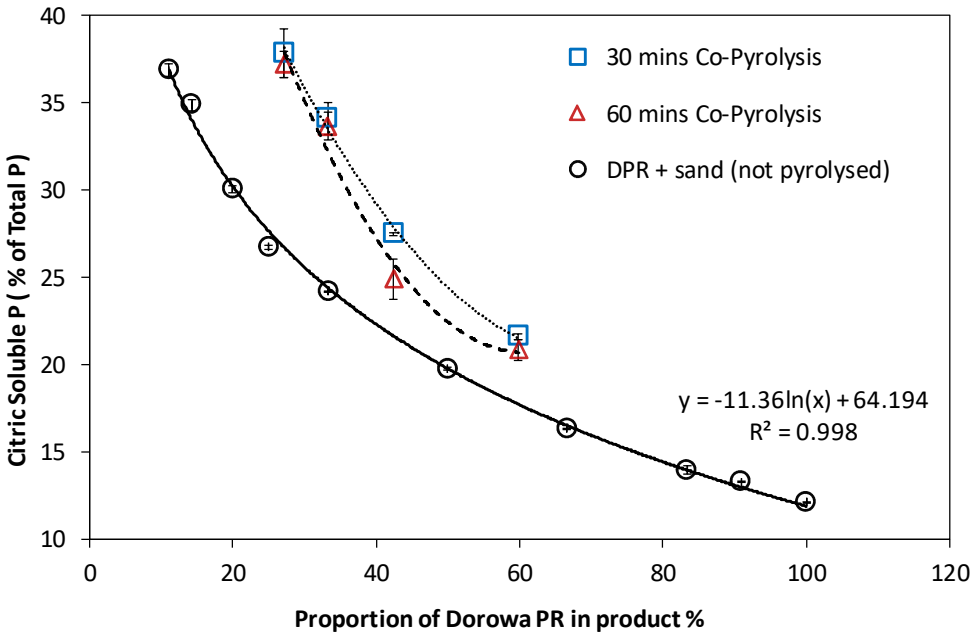

Figure 5.6 Comparison of citric soluble P of biochar products with unamended DPR. Error bars represent 2x standard error of means (SEM), n =3

This comparison allowed us to evaluate the change in citric solubility compared to the DPR at the same solid/solvent and P/solvent ratios. The solid/ solvent and P/ solvent ratios are known to affect the amount of P solubilised in extractants such as citric acid (Camps-Arbestain *et al.*, 2017). Only the 1:8 and 1:6 (DPR/ maize) premixes produced biochars with more than a 30% increase in citric-soluble P compared to the unamended DPR. The effect of increasing the residence time from 30 to 60 min was not significant in improving the citric-soluble P of the 1:8 and 1:6 initial mixes.

Hypothetical P removal by maize yielding 13 tonne ha^{-1} at the end of the growing season is around 45 kg P ha^{-1} (not taking into account soil type and growth conditions) (Camps-Arbestain *et al.*, 2015). In order to supply about 40 kg of citric-soluble P using the biochar produced from the 1:8 and 1:6 DPR + maize mixes, about 2.4 and 2.2 tonne, respectively, of the biochar product would be required when the pyrolysis residence time is 30 min. At the same respective mixing ratios and for 60 min residence time, 2.3 and 2.1 tonne would

suffice. To produce 2.1 tonne of biochar from a 1:6 DPR + maize mixture, about 4.5 tonne of oven-dried maize residue (stems + leaves) would be needed together with 750 kg of the DPR.

5.4 Conclusions

Co-pyrolysis of waste maize stover with a low solubility igneous PR significantly increased the amount of PR-P that was bio-available as measured by citric acid extraction. In addition, co-pyrolysis with the DPR increased C and N retention in the biochar by up to 43 and 26%, respectively. Addition of the DPR to the maize stover prior to pyrolysis also improved the lime value of the final biochar. On farm, co-pyrolysis of crop waste with otherwise less-soluble PRs has the potential to produce low-cost P fertilisers with potential for liming and adding C to acidic soils for economically challenged smallholder farmers. Glasshouse and field studies are recommended to assess the agronomic effectiveness and the C sequestration potential of these and similar BBFs. Further studies on the stability of the retained C and N in the biochars and the mechanisms by which citric P solubility is increased are recommended.

The outcome of this chapter achieves the third objective of the thesis, which was to assess the effect of co-pyrolysis of maize stover with DPR on P solubility, liming value and recovery of C from biomass and DPR.

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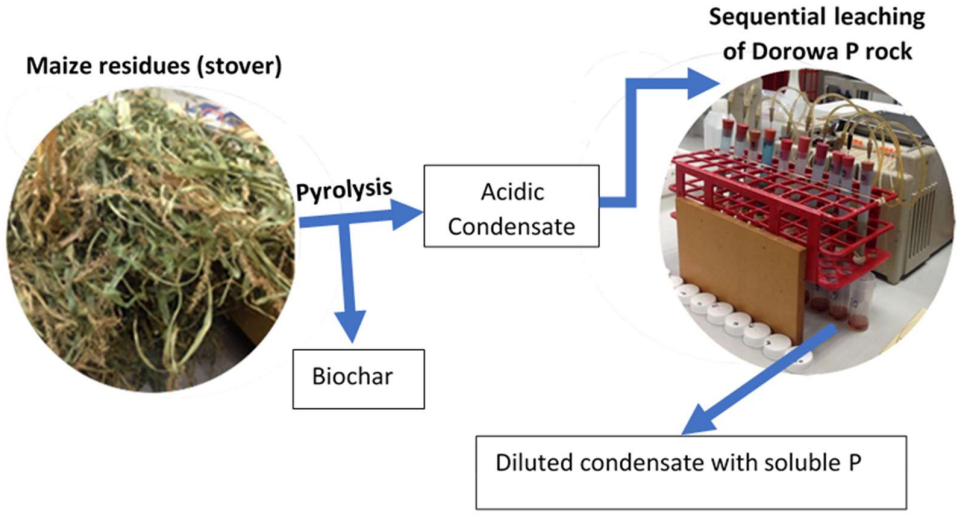
CHAPTER 6

AGRONOMIC PHOSPHORUS RECOVERY FROM AN IGNEOUS PHOSPHATE ROCK USING PYROLYSIS CONDENSATE

The previous chapter (chapter 5) discussed the use of a pyrolytic process to produce a potential biochar-based P fertiliser while the use of the liquid fraction by-product was not discussed. In this chapter, the potential of condensate from the pyrolysis of maize stover is explored as a relatively low-cost organic acid source for recovering P from the Dorowa PR. The thrust of this chapter was towards the realisation of multiple benefits by using pyrolysis condensate from a system producing biochar for soil melioration.



Abstract

Directly applied igneous phosphate rocks (PR) are agronomically ineffective because they are intrinsically unreactive. The main process by which PRs are solubilised in soils by microbes and plants is through the exudation of low molecular weight organic acids, which have a short lifespan in soils, thereby limiting the period of PR dissolution and agronomic effectiveness. This study measured the amount of P recovered from Dorowa PR (DPR) by suspension in and sequential leaching with citric, acetic, oxalic acids, and pyrolysis condensate at various pH values. Of the dilute acids tested, oxalic acid was more effective at solubilising P from the DPR, cumulatively liberating 46% of total P from the DPR after 3 extractions at pH 3. However, aqueous phase pyrolysis liquid from maize stover pyrolysis was less effective at recovering P, yielding less than 14% of the total P despite maintaining a pH range of 3 to 3.8 in leachates after sequential extractions. The poor solubilisation was due to the low concentrations of chelating and complexing acids in the pyrolysis liquid, with the dominant acid being acetic acid. Research on other alternative processes to produce complexing acids such as oxalic acid is recommended.

6.1 Introduction

Direct application phosphate rocks (PR) of high chemical reactivity (carbonate substituted apatites) have proved to be effective P fertilisers for pastures in acid soils (Bolan and Hedley, 1989; Bolan and Hedley, 1990; Bolan *et al.*, 1993). Significant activity of microbial processes in soils that facilitate the oxidation of reduced carbon, nitrogen, and sulphur compounds in acid soils are often sufficient to maintain soil pH below the equilibrium pH at which carbonate substituted apatites dissolve (Bolan and Hedley, 1990; Rajan *et al.*, 1991). The less reactive PRs (e.g. igneous PR) such as the Kodjari PR from Burkino Faso (Fukuda *et al.*, 2013; Nakamura *et al.*, 2020) and the Dorowa PR (DPR) from Zimbabwe (Tumbure *et al.*, 2020; Govere *et al.*, 2005), however, do not dissolve sufficiently to provide plant available P when directly applied to soils. Therefore, where soluble P fertiliser manufacturing facilities are not available, or run at a high cost, researchers have evaluated biological acidulation processes, such as using sulphur oxidising bacteria (Biosuper, (Rajan, 1982a; Rajan, 1983; Rajan, 1982b) and composting (Mupondi *et al.*, 2018; Kpomblekou and Tabatabatai, 1994; Yadav *et al.*, 2017) to assist with the solubilisation of PRs.

In-situ microbial solubilisation of PRs in soils has been of interest to researchers for a considerable time (Sperber, 1957; Moghimi *et al.*, 1978; Kootstra *et al.*, 2019; Rajan and Edge, 1980). The effectiveness of microorganisms to solubilise PRs hinges on the production and exudation of organic acids, which is strongly influenced by environmental and nutritional parameters controlling microbial populations (Jha *et al.*, 2018). This presents great challenges in optimising microbial solubilisation in drier, impoverished soils that support limited microbial diversity and activity. The major mechanism by which microbes solubilise P is through exudation of low molecular weight organic acids

(LMWOA), which chelate those cations bound to phosphate (Nobahar *et al.*, 2017; Kootstra *et al.*, 2019). These LMWOAs are readily available C substrates, have a low persistence in soil (Roy *et al.*, 2016) and are as weak acids, generally neutralised by the soil's pH buffering capacity (Aria *et al.*, 2010), rather than accelerating PR dissolution.

Ex-situ solubilisation of PRs with organic acids produced from separate optimised processes, such as fermentation (Qiao *et al.*, 2019; Chen *et al.*, 2015; Kobayashi *et al.*, 2014; Li *et al.*, 2016) and pyrolysis (Theapparat *et al.*, 2015; Li *et al.*, 2018) have the potential to solve the problems of in-situ solubilisation. In previous studies by Kpomblekou and Tabatabatai (1994), the most effective low molecular weight organic acids that solubilised P from PRs were found to be citric, cis-aconitic, and oxalic acids. Recent work by Mendes *et al.* (2020) found that oxalic acid was more efficient at solubilising P than sulphuric acid across a range of reactive and non-reactive PRs. With biochar production being promoted as a greenhouse gas (GHG) mitigation and soil nutrient loss-curbing technology (Yadav *et al.*, 2019; Yang *et al.*, 2019), then pyrolysis condensate produced from the pyrolysis of biomass (Theapparat *et al.*, 2015) may also be a significant source of low molecular weight organic acids. Pyrolysis is the thermochemical conversion of organic biomass to biochar (and its associated by-products) in the absence of oxygen (Libra *et al.*, 2014). The final products of the pyrolytic process are char (solid), condensate (liquid comprising various organic compounds and condensed gases), and non-condensable exhaust gases. Most pyrolysis research in agriculture has focused on obtaining biochar from slow-pyrolysis processes, with the final aim of soil amelioration (Fuertes *et al.*, 2010). Less research has focused on the beneficial use of the liquid fractions. For example, as a potential chelator of heavy metals in

contaminated soils (Benzon and Lee, 2017), and as potential plant and microbial stimulants (Luo *et al.*, 2019).

Within the aqueous pyrolysis liquid fraction are dissolved organic compounds such as furfural, hydroxymethylfurfural (HMF), organic acids, aldehydes, and phenols (Fuertes *et al.*, 2010; Libra *et al.*, 2014). The non-aqueous "oil" fraction contains insoluble organics (mainly aromatics) of high molecular weight (Demirbas and Balat, 2006). Disposal or use of the aqueous phase is limited by the toxic nature of some of the products such as HMF, furfural, and aldehydes. The separation of these components is a daunting task, and the use of classic thermal separation processes, such as distillation, is ineffective (Machado *et al.*, 2018). Research to establish practical techniques to isolate undesirable chemicals from the liquid pyrolysis fraction is still in its infancy. Keskinen *et al.* (2017) explains that effective methods have not yet been developed, and new ways to utilise pyrolysis by-products in the liquid phase are needed.

Using the pyrolysis condensate as an acid source for PR solubilisation would only require separating the oil and aqueous fraction. This study aimed to evaluate P recovery from Dorowa PR (DPR) using the aqueous phase of pyrolysis liquid produced from corn stover pyrolysis. The feasibility of P recovery from DPR was first evaluated using extraction and/or leaching with dilute acetic, citric, and oxalic acids to various pH endpoints. This was followed by sequential leaching experiments with diluted pyrolysis liquid. It was hypothesised that the extent of P release in the weak acid solution would depend upon the extent of proton supply to the phosphate at differing solution pH. The second hypothesis was that the mixture of organic acids in the aqueous phase of pyrolysis liquid could significantly solubilise P from DPR and sequential extractions would improve P recovery.

6.2 Materials and methods

6.2.1 Samples

The sampling and characterisation of the DPR and the maize residues used in this study are described elsewhere (Tumbure *et al.*, 2020; Tumbure *et al.*, 2019) and in section 5.2.1 of Chapter 5.

6.2.2 Initial dissolution / titration experiments using pure dilute acids

Suspensions of DPR: DI water (0.5g/ 50mL) were shaken overnight in 100 mL polyethylene screw top containers and left to stand for a further 48 hours to ensure equilibration of the suspension. End point titrations (replicated 3 times for each endpoint and type of acid) were then performed using a TitraLab® 865 auto-titrator, with the temperature set at 25 ± 0.5 ^{o}C and stirred at 600 rpm. The auto-titrator was programmed to allow 10 min for equilibration before initial pH was measured, and titration only began when a stable pH reading had been reached. The burette delivery speed was set between 0.01 and 0.02 mL/min, with proportional control employed to improve accuracy of the end point. An end point delay of 30 min was used to ensure equilibration at the final pH. Endpoint pH values were set to 6, 5, 4, and 3, for the samples, and titrations were performed using 0.1 M of either sulphuric, citric, acetic, or oxalic acid. An acid concentration of 0.1M was used to simulate the low concentration of organic acids in the diluted aqueous phase of the pyrolysis condensate. This concentration was in the mid-range of the study by Mendes *et al.* (2020) to assess PR dissolution using various acids. When pH endpoint equilibria were reached, samples were immediately extracted and filtered through a 0.45 µm Millipore® Nitrocellulose filter paper under suction.

Selected cation concentrations in the filtrates obtained after each extraction were measured using atomic emission spectrophotometry (AES) on an Agilent® 4200

MPAES. To improve accuracy, matrix matching was employed for the standards, and spiked standards were included. The P content in the filtrates was measured following the addition of a vanado-molybdate reagent by UV-vis spectrophotometry after diluting a 10 ml aliquot of each filtrate into 250 mL volumetric flasks (Fertmark, 2016).

The acids were ranked according to how much they solubilised the DPR and the top 2 acids were selected for sequential titrations. For these titrations, the residue left on the filter paper was washed with DI water and then resuspended in 50 mL of DI water. The titration was then repeated to the same pH end point. Washing of residue, and re-suspension and titration to the same pH endpoint, was repeated three times. The same leachate analytical procedures as previously mentioned for determination of P, and selected cations in leachates were employed.

6.2.3 Production, processing and characterisation of pyrolysis liquid

A pyrolysis reactor composed of a rotating 25 L drum and LPG heating was used (Plate 1). Exactly 2 kg of maize stover (stem + leaves), previously dried at 70 ^{o}C and ground to less than 2 mm diameter, was placed in the reactor. Pyrolysis was performed by heating to 300 ± 10 ^{o}C and maintained until production of exhaust gases ceased, indicating completion of pyrolysis. This pyrolytic process produced biochar and pyrolysis condensate that was 39.2 and 35.6% respectively, of the initial maize stover mass (2 kg). The pyrolysis condensate was mixed with DI water in ratios of 1:4 and 1:1 (condensate/ water), and left overnight at 4 ^{o}C, after which the solutions were centrifuged at 5000 rpm for 5 min, and then decanted to collect the aqueous phase pyrolysis liquid.

The pH of the aqueous phase pyrolysis liquid was measured using a Thermo Scientific Orion Star A214 pH meter, and the total acid number (TAN) was measured

potentiometrically by titrating with 0.1M KOH on a TitraLab® 865 autotitrator. The TAN analysis is an accepted method for pyrolysis condensate, originally developed (and adapted) from the measurement of the acidity of petroleum products (Park *et al.*, 2017). Organic acids in the aqueous-phase pyrolysis liquid were identified and quantified by reversed phase liquid chromatography (RP-HPLC) using a Dionex ultimate 3000® HPLC. The HPLC was equipped with a Luna® C18 (2), 250 mm x 4.6 mm column and a 25 mM KH_2PO_4 (at pH 2.5) mobile phase (Cawthray, 2003).

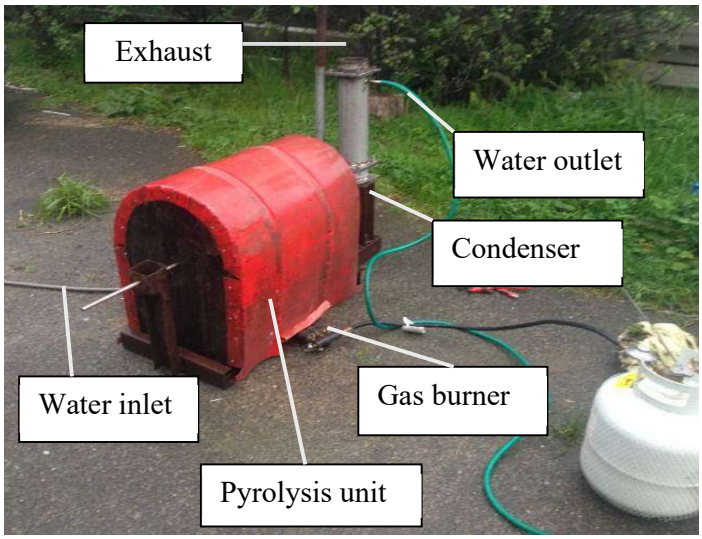


Plate 6.1 25L Covered rotating drum pyrolytic reactor

6.2.5 Column leaching of DPR with aqueous phase pyrolysis liquid

A column leaching study was performed using DPR that was mixed with acid washed sand at a ratio of 0.5 g DPR: 7.5 g sand per leaching tube. Leaching tubes were made of polythene, had a volume of 11.5 mL, a height of 130 mm, and an open-end internal diameter of 12 mm. The bottom of the column consisted of a fiberglass filter paper to prevent loss of the column contents during the leaching process. Leaching tubes were tapped to ensure consistent bulk density, and all leaching tubes were initially moistened to approximately field capacity using 1.3 mL of pyrolysis liquid (diluted either 1:4 or 1:1)

and left to stand for 2 hours. Sequential leaching was then performed by delivering the aqueous phase pyrolysis liquid at a rate of 0.05 mL/ min by means of a peristaltic pump. Leachate was collected into pre-weighed containers after 2, 4, 6, 8, 12, 18, and 26 hours. A set of 4 replicates were run, with a blank consisting of acid washed sand only.

6.2.6 Chemical analysis of the pyrolysis liquid leachate

The pH of the collected leachates was measured using a Thermo Scientific Orion Star A214 pH meter. For analysis of P and other element concentrations in solution, a 2 mL aliquot of the leachate was first digested in 10 mL of 70% HNO_3 to remove organics which could interfere with measurements. The P, Ca, Mg, Na, Al, Fe, and Mn content of the digested leachates was analysed as previously mentioned in section 6.2.2.

6.3 Results and discussion

6.3.1 Dissolved P and selected elements from single dilute acid extractions

Irrespective of the type of extracting acid, when pH set points ranged from 6 to 4, less than 3 % of the total P present in the DPR was solubilised (Figure 6.1a). When the pH was lowered to 3 by titrating with oxalic, citric, and sulphuric acids, 14.0, 7.4, and 4.7% of the total P present in DPR was dissolved, respectively. Oxalic acid liberated the highest amount of P compared to the other acids. When the pH was 3, the final concentration of oxalic acid in the PR suspension was 12 mmol/ L, similar to the 10 mmol/ L concentration used by Kpomblekou and Tabatabatai (1994), who also found that oxalic acid mobilised the greatest amount of P (4 – 5 g kg^{-1} PR) from Kodjari and North Florida PRs compared to a range of other organic and mineral acids.

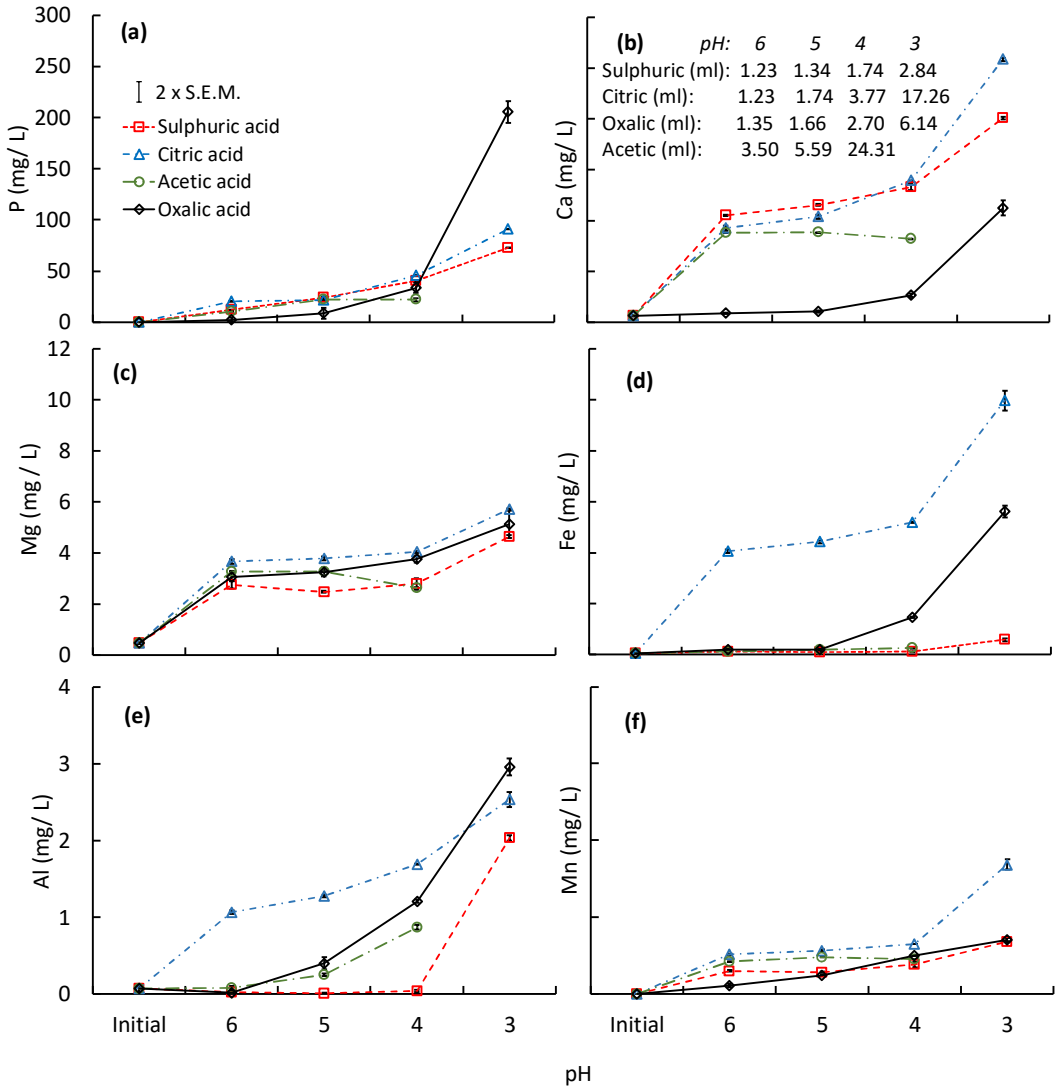


Figure 6.1 Concentration of P **(a)**, Ca **(b)**, Mg **(c)**, Fe **(d)**, Al **(e)** and Mn **(f)** extracted from DPR using various dilute acids. Table in **(b)** shows volume of acid titrated to each pH end point.

With the exception of the oxalic acid extracts, the concentration of Ca in all acid extracts was at least 2.5x higher than that for P from pH 6 to 3 (Figure 6.1b). Oxalic acid extracts had similar P and Ca dissolution trends from pH 6 to 4, but at pH 3, the concentration of P was about twice that of Ca. This trend is consistent with the chemical behaviour of Ca in oxalate solutions at low pH, in other studies where varied P sources such as PRs,

sewage incineration ash, and pig manure ash, were reacted with oxalic acid, with the resulting precipitation of insoluble oxalate salts (Liang *et al.*, 2019; Kootstra *et al.*, 2019; Sagoe *et al.*, 1998). Other researchers explain that the ability of organic acids to remove Ca from the solution via precipitation is more significant for increasing P dissolution compared to chelation and/or protonation (Kootstra *et al.*, 2019; Basak, 2018; Sagoe *et al.*, 1998).

In comparison to other acids, higher concentrations of dissolved Fe, Ca, Mg, and Mn, were generally obtained when citric acid was used, while sulphuric acid produced the lowest concentrations of Mg, Fe, and Al (Figure 6.1c, d, e). Lazo *et al.* (2017) report similar findings for iron phosphate where citric acid dissolved twice as much Fe phosphate compared to when oxalic acid was used.

Generally, the Ca:P molar ratios in sulphuric, citric, and acetic acids closely followed each other (Figure 6.2 a). However, for oxalic acid, the Ca:P molar ratio was at least 3 times less than that of other acids from pH 5 to 3 (Figure 6.2a). Kpomblekou and Tabatabatai (1994) also reported similar differences in the Ca:P molar ratio in solution when 10 mM citric and oxalic acid extractions were used to solubilise Kodjari and North Florida PR. A relatively higher Ca:P molar ratio was observed for all acids at pH 6 which gradually declined as the pH was reduced to pH 3. The high Ca:P molar ratio at pH 6 for all acids is because more calcite than apatite was solubilised at these higher pH values (Tumbure *et al.* (2019), see Chapter 3, section 3.3.2).

The effects of different processes (protonation, chelation, complexion) in acid action were inferred from (Al or Fe): P molar ratios in the acid extracts. Protonation and or chelation

increased Al in solution for sulphuric and acetic acids, while insoluble or sparingly soluble Al-complex formation in oxalic acid reduced Al in solution.

Citric acid had the highest Fe:P molar ratios at each pH (Figure 6.2b), while acetic and sulphuric acids had very low Fe:P molar ratios. The ability of citric acid to chelate relatively more Fe into solution can be attributed to its β-hydroxyl group which forms chelated six-member ring structures with Fe (Chatterjee *et al.*, 2015). Citric and oxalic acids had their highest Al:P molar ratios at pH 5 which steeply declined with a reduction of pH up to pH 3 (Figure 6.2c). This suggests that at pH 5 oxalic and citric acids dissolved mostly non-apatite Al as confirmed by low P dissolution at that pH. At the same time, sulphuric acid had the lowest Al:P molar ratio at pH 6 to 4 which then increased at pH 3. This is because the mechanism by which sulphuric acid dissolves Fe and Al bound to apatite or gangue minerals is through protonation which becomes less effective at higher pH values.

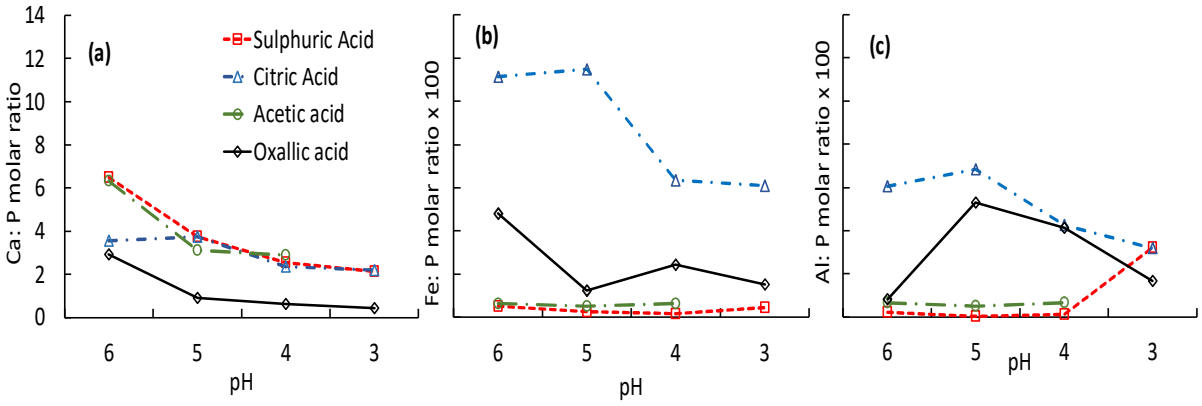


Figure 6.2 Molar ratio relationship between solubilised P and Ca **(a)**, Fe **(b)** and Al **(c)** after extraction from DPR using various acids

6.3.2 Dissolved P and selected elements from sequential dissolution in citric and oxalic acids

Following the titration experiments reported in section 6.3.1 above, citric and oxalic acids were selected for sequential extractions since they solubilised relatively more P than acetic and sulphuric acids. Low amounts of P were solubilised by citric acid at pH > 4, resulting in solution concentrations of less than 20 mg/ L (Figure 6.3a).

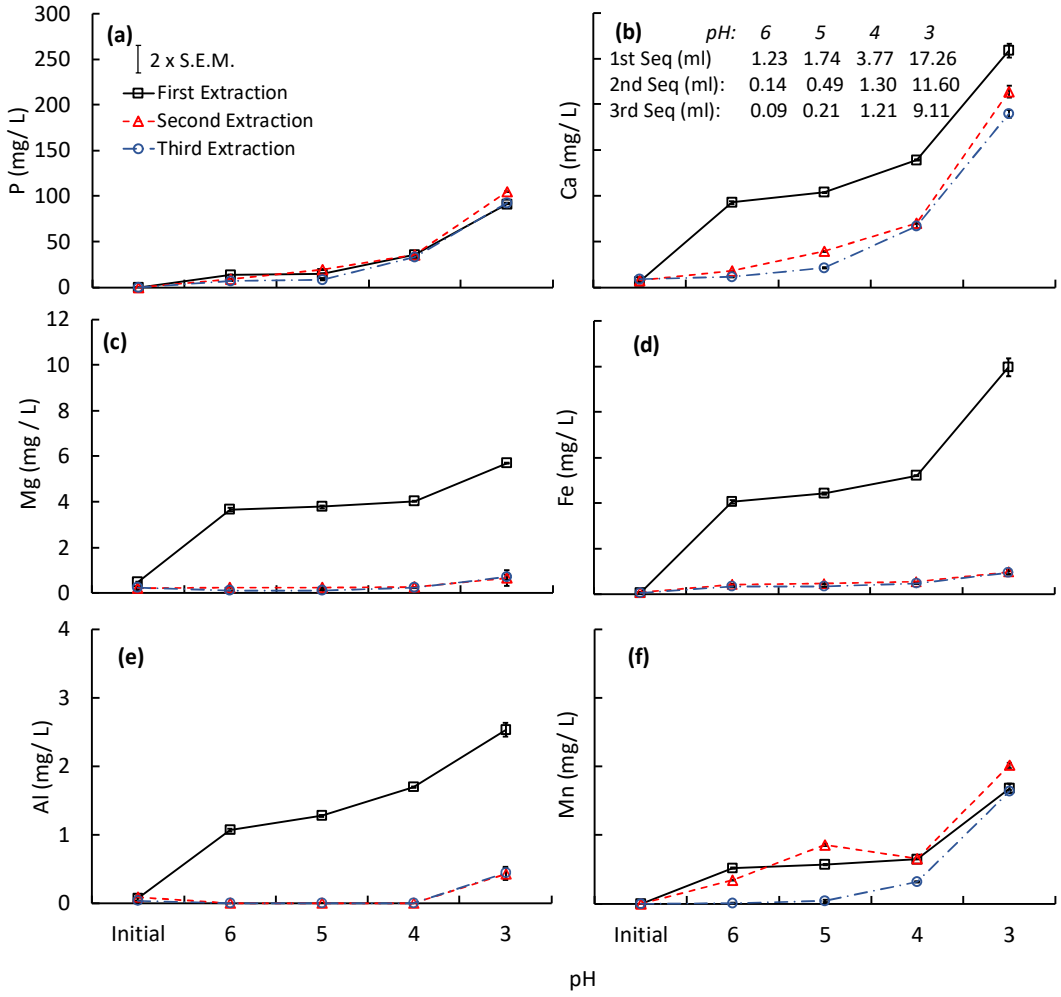


Figure 6.3 Concentration of P **(a)**, Ca **(b)**, Mg **(c)**, Fe **(d)**, Al **(e)** and Mn **(f)** sequentially extracted from DPR by titrating against 0.1M citric acid. Table in **(b)** shows volume of citric acid titrated to each pH end point.

However, at pH 3, about 7.4, 7.8, and 6.6% of the total P content in DPR was solubilised by the first, second, and third sequential extractions using citric acid, respectively, giving a total P extraction value of 21.9%. The near-similar amount of P that was solubilised by citric acid at each sequential extraction at pH 3 implies that further extractions beyond the third could continue to recover significant amounts of P, although at diminishing rates. Extraction of similar amounts of P from DPR have been previously reported after two sequential extractions with a fixed amount of 2% citric acid (Tumbure *et al.*, 2019).

Concentration of Ca in citric acid extracts at pH 3 reduced by about 17 and 26 % in the second and third sequential extractions, respectively (Figure 6.3b). The amount of Ca observed in extracts at pH 3 was 9, 7, and 6 % of the total Ca in DPR for the first, second and third sequential extractions respectively. The higher amount of Ca solubilised in the first extraction is because a part contribution of this is from calcite present in the DPR, which becomes much less in subsequent extractions.

Compared to other citric acid extractions, the first extraction gave the highest concentration of Mg, Fe and Al from pH 6 to 3 (Figure 6.3c, d, e). At pH 3 the amount of Mg and Al solubilised from the first extraction was >21 % of the content in DPR while the second and third extractions solubilised about 3% of Mg and Al content in DPR. The amount of solubilised Fe showed the same trend at pH 3, with about 14 % of Fe in DPR solubilised in the first extraction and 1% solubilised in succeeding extractions. The reason for this trend is that, in the first extraction, the dissolution of apatite, calcite, and other gangue minerals, all contribute to elements in solution, and non-apatite constituents in DPR may be relatively more rapidly dissolved during the first extraction.

From pH 6 to 4, each oxalic acid sequential extraction did not exceed a P concentration of 35 mg P/ L (Figure 6.4a), which constituted, at each extraction, less than 2.2% of the total P in DPR. As expected, the highest solubilised P was at pH 3, which maintained a concentration of at least 205 mg P/ L at each sequential extraction (Figure 6.4a). Sequential extractions of oxalic acid at pH 3 solubilised 14.0, 16.1, and 16.2% of the total P in DPR for the first, second, and third, sequential extractions, respectively, totalling 46.3% of the total P in DPR.

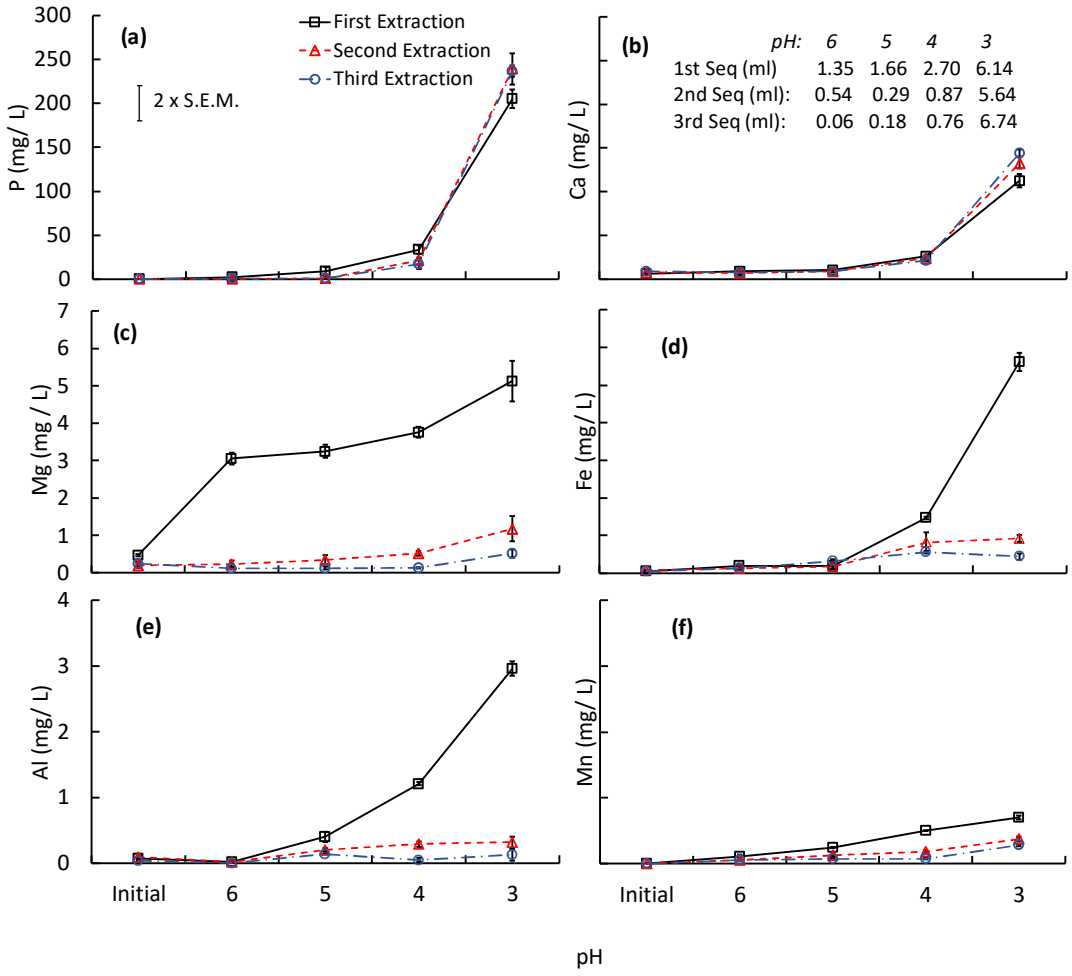


Figure 6.4 Concentration of P **(a)**, Ca **(b)**, Mg **(c)**, Fe **(d)**, Al **(e)** and Mn **(f)** sequentially extracted from DPR by titrating against 0.1M oxalic acid. Table in **(b)** shows volume of oxalic acid titrated to each pH end point.

Given that the amount of P solubilised in the second and third extractions were the same, we speculate that if sequential extractions had been continued, nearly 100% of the P in the DPR could have been recovered, as has been observed when PR's were extracted with oxalic acid by Mendes *et al.* (2020).

Solubilised Ca, Fe, Al, Mg, and Mn is described for pH 3 only, since that is where the highest amount of P was solubilised. At pH 3, oxalic acid Ca had a concentration of between 112 – 144 mg Ca/ L for the three sequential extractions (Figure 6.4b) which was about half the concentration of P in solution. The amount of Ca present in three sequential extractions of oxalic acid at pH 3 was 11.8% of the Ca amount in DPR (37.1%) (Tumbure *et al.*, 2019). The Ca:P molar ratio for the same three extractions ranged from 0.42 to 0.47. This shows that oxalic acid solubilised apatite P and Ca and was able to keep some of the Ca out of solution at the same level of effectiveness regardless of extraction sequence. The first extraction had higher concentrations of Mg, Fe, Al, and Mn, compared to subsequent extractions (Figure 6.4c, d, e, and f). During the first oxalic acid extraction at pH 3, about 6.5, 19.5, 18.6, and 19.6%, of the total Fe, Al, Mg, and Mn was solubilised, respectively. This is likely from part contributions of gangue minerals in Dorowa PR which do not correlate with P dissolution. Both the second and third extractions solubilised less than 2.1% each of the total Fe and Al. Low levels of Fe and Al would be advantageous for soil application because of less risk of forming insoluble Fe and Al phosphates in soil. The Fe:P and Al:P molar ratio for each of the three extractions was less than 0.03.

6.3.3 Practicality of oxalic acid and citric acid sequential extractions

Hypothetically, a maize plant requires about 1 g of P per plant (45 kg P ha^{-1}; (Camps-Arbestain *et al.*, 2015), 45 000 plants ha^{-1}). If plant recovery of applied P is about 33%,

this means that 3 g of P/plant would need to be applied to the root zone. The oxalic acid titration mix, consisting of about 220 mg P/ L, would require 13 L/ plant of the mix which is about 20% of the water needed to grow a maize plant to physical maturity. It would be necessary to reduce the amount of water used in the leaching of DPR, so the initial water addition step could be omitted, and the concentration of oxalic acid increased to make volumes more practical. At 56 mL/ 0.5 g DPR and 3 oxalic acid extractions per 0.5 g DPR, a single maize plant would require 39 g of DPR and 1.6 L of 0.1M oxalic acid (containing 13.5 g of pure oxalic acid). The general high cost of industrial oxalic acid (~ 800€ /t) is four times that of sulphuric acid (Kootstra *et al.*, 2019), and discourages the prospect of using oxalic acid. The mixture of organic acids in the pyrolysis liquid would be cheaper to produce and may provide significant protonation, chelation, and complexing processes, aiding the dissolution of P in the DPR. This provides the context for assessing the P-solubilisation power of aqueous phase pyrolysis liquid.

6.3.4 Selected organic acid composition and acidity of aqueous phase pyrolysis liquid

Collected crude pyrolysis condensate from the pyrolysis of maize stover was 35.6% of the initial feedstock mass, and the decanted aqueous phase pyrolysis liquid (1:4 crude liquid to water) had a pH of 2.94 and total acid number of 25.7 mg KOH/ g. The observed pH and TAN was in the range to that reported by other researchers (pH 3, TAN 20.1 – 30.1) for a crude pyrolysis condensate/ water mixture (1:4) obtained from switchgrass pyrolysis (Ren and Ye, 2018; Ren *et al.*, 2016). It should be noted that TAN can slightly overestimate total acid content because phenolic compounds are also neutralised with KOH (Oasmaa and Meier, 2005).

An acetic acid concentration of 0.41 moles/ L was the highest of the seven organic acids analysed in the pyrolysis liquid (1:4 mixture) (Table 6.1). Other researchers report that acetic acid is usually the most dominant acid in pyrolysis condensate from fast pyrolysis or hydrothermal carbonisation of biomass (Reza *et al.*, 2014; Keskinen *et al.*, 2017; Kambo *et al.*, 2017). Oh *et al.* (2017) explains that acetic acid in pyrolysis condensate is derived from the breakdown of the hemicellulose component in the feedstock. Citric and tartaric acids were not identified in the aqueous phase pyrolysis liquid, and oxalic acid concentrations were relatively low (0.04 M). The acetic acid concentration in the diluted pyrolysis condensate (1:4) was higher than the 0.1M concentration of the laboratory-grade acid used in titrations (Section 6.3.1), while the concentration of oxalic acid was lower in the pyrolysis condensate. As a result, enhanced leaching with acetic acid in the condensate was expected.

Table 6.1 Concentration of selected organic acids in aqueous phase pyrolysis liquid that was diluted at 1:4 (condensate/ water)

Organic acid	**Concentration (moles/L)**
Oxalic	0.038 ± 0.011
Tartaric	0
Malic	0.017 ± 0.005
Acetic	0.410 ± 0.022
Maleic	0.003 ± 0.0002
Citric	0
Succinic	0.099 ± 0.004

Numbers after ± are standard errors of means (SEM)

6.3.5 Solubilised P and other selected elements after sequential leaching of DPR with aqueous phase pyrolysis liquid

The concentration of P in pyrolysis liquid leachates ranged from 102 to 253 mg P/ L at each leaching stage for both the 1:1 and 1:4 pyrolysis liquid mixtures, representing about 0.87 to 3.17% of the total P solubilised from DPR after each stage (Figure 6.5).

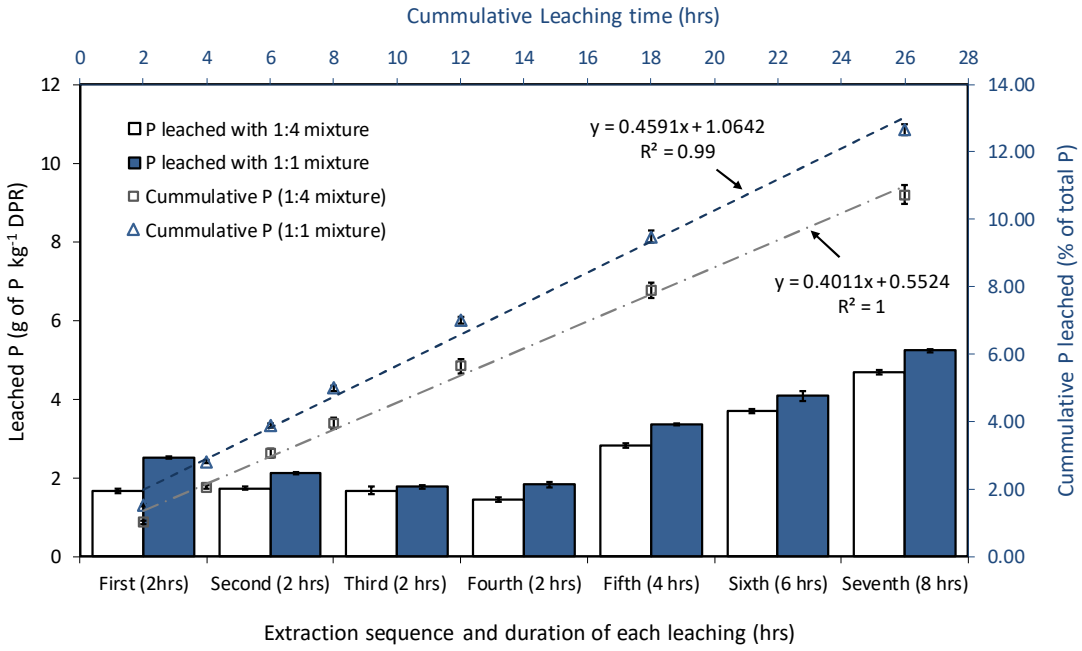


Figure 6.5 Amount of P sequentially extracted from DPR using pyrolysis condensate mixed at 1:1 and 1:4 (condensate/ water) ratios. Error bars represent 2x standard errors of means (*n = 4*)

Compared to titrations with pure acids at pH 3, sequential leaching with aqueous phase pyrolysis liquid solubilised considerably less P while maintaining a pH of 3. There was a linear relationship ($R^2 > 0.99$) between the cumulative amount of P leached and the cumulative leaching time for both the pyrolysis liquid ratios. The aqueous phase pyrolysis liquid diluted at 1:1 leached about 18% more P than when a pyrolysis liquid mixture of 1:4 was used. However, this cumulatively translated to only 2% more of the total P solubilised after 26 hrs (Figure 6.5). This suggests that the effect of varying acid

concentration (affecting H^+ supply) in the aqueous phase pyrolysis liquid extracts had a reduced effect on P dissolution. The low amount of P cumulatively leached over 26 hours suggests that use of pyrolysis liquid to solubilise P from DPR may be ineffective. The low concentration of strong acid complexing agents such as oxalic and citric acids is likely the reason why P dissolution was low (Section 6.3.4). All leachates had low pH (2.99 – 3.84) with the highest pH recorded in the first 2 hours of extraction (Table 6.2). A final pH of around 3 did not improve P dissolution compared to that observed during previous titrations with pure acids (Section 6.3.1). It is likely that this pH value is influenced or buffered by other constituents in the aqueous phase pyrolysis liquid and does not correlate well with its ability to extract P from apatite.

The highest concentration of Ca, Mg, Fe, and Mn were recorded after the first 2 hours of leaching. An option to discard the first 2 hours of leachate is therefore possible, to remove considerable quantities of Fe and Mn, which could react with P and make it unavailable upon soil addition. The concentration of Ca in the leachate collected in the first 2 hours was at least 3.5x that of the succeeding leachates. After 26 hours of sequential leaching, at least 42, 12, 6, and 11% of the total content of Mg, Ca, Fe, and Al in DPR respectively, had been leached by both of the aqueous phase pyrolysis liquid ratios used.

The Ca:P molar ratio of leachates at 2 hours was > 4.3 for both pyrolysis liquids (Figure 6.6a). This indicated that considerable quantities of calcite were solubilised together with apatite in the first leaching (Tumbure *et al.*, 2019). Succeeding extractions had a Ca:P molar ratio that was around 1.5, a value that was less than that observed for dilute sulphuric and citric acids at pH 3 (Section 6.3.1), indicating relatively incongruent dissolution where P was preferentially released over Ca.

Table 6.2 Cation content and pH of pyrolysis liquid leachates after sequential leaching of DPR

	Leached with 1:4 aqueous phase pyrolysis liquid								Leached with 1:1 aqueous phase pyrolysis Liquid							
Time (hr)	**Vol (mL)**	**pH**	**Ca (mg/L)**	**Mg (mg/L)**	**Fe (mg/L)**	**Al (mg/L)**	**Mn (mg/L)**		**Vol (mL)**	**pH**	**Ca (mg/L)**	**Mg (mg/L)**	**Fe (mg/L)**	**Al (mg/L)**	**Mn (mg/L)**	
2	4.62 ± 0.08	3.84 ± 0.02	1242.42 ± 17.36	29.30 ± 0.70	15.08 ± 1.19	3.67 ± 0.77	5.23 ± 0.20		5.01 ± 0.11	3.39 ± 0.05	1416.56 ± 20.54	28.13 ± 1.49	35.16 ± 0.92	8.36 ± 0.23	5.78 ± 0.20	
4	5.09 ± 0.14	3.41 ± 0.13	361.56 ± 16.48	5.55 ± 0.23	10.23 ± 0.84	3.98 ± 0.41	0.94 ± 0.13		5.41 ± 0.10	3.08 ± 0.01	360.31 ± 9.11	3.83 ± 0.15	9.45 ± 0.23	2.42 ± 0.27	0.63 ± 0.00	
6	5.37 ± 0.14	3.19 ± 0.03	289.61 ± 2.73	2.19 ± 0.22	7.03 ± 0.30	2.58 ± 0.08	0.31 ± 0.00		5.64 ± 0.11	3.03 ± 0.03	303.20 ± 14.78	1.88 ± 0.13	9.84 ± 0.37	1.64 ± 0.20	0.31 ± 0.00	
8	5.39 ± 0.12	3.05 ± 0.04	259.61 ± 5.16	1.56 ± 0.00	3.67 ± 0.35	1.17 ± 0.08	0.00 ± 0.00		5.65 ± 0.12	2.93 ± 0.03	282.11 ± 2.36	1.48 ± 0.08	5.00 ± 0.60	1.17 ± 0.15	0.31 ± 0.00	
12	11.24 ± 0.24	3.17 ± 0.01	249.84 ± 6.66	1.02 ± 0.08	2.81 ± 0.34	0.94 ± 0.13	0.00 ± 0.00		11.83 ± 0.23	2.99 ± 0.04	263.75 ± 5.48	0.78 ± 0.09	2.81 ± 0.26	1.02 ± 0.15	0.31 ± 0.00	
18	17.04 ± 0.37	3.03 ± 0.01	224.30 ± 4.61	0.70 ± 0.08	1.80 ± 0.15	0.55 ± 0.08	0.00 ± 0.00		16.77 ± 0.77	2.92 ± 0.01	238.59 ± 1.52	0.63 ± 0.00	2.58 ± 0.15	0.70 ± 0.20	0.00 ± 0.00	
26	23.26 ± 0.57	3.14 ± 0.01	194.30 ± 9.27	0.70 ± 0.08	2.03 ± 0.39	0.47 ± 0.09	0.31 ± 0.00		19.41 ± 0.77	3.03 ± 0.00	204.30 ± 10.36	0.70 ± 0.20	3.20 ± 0.35	0.16 ± 0.09	0.00 ± 0.00	
Total (% of elemental content)			**11.68**	**14.42**	**5.89**	**11.02**	**19.39**				**12.63**	**13.81**	**9.18**	**12.21**	**20.24**	

Figures after ± are standard errors of means (SEM), n=4

This is likely because of Ca complexation reactions, albeit at a much lower degree than observed previously (Section 6.3.2) for oxalic acid titrations. The succinic acid contained in the pyrolysis condensate is likely to have contributed a small percentage to Ca complexing reactions because it is a much weaker acid than oxalic acid (pK_{a1} 4.61 and 1.25 for succinic and oxalic acids, respectively).

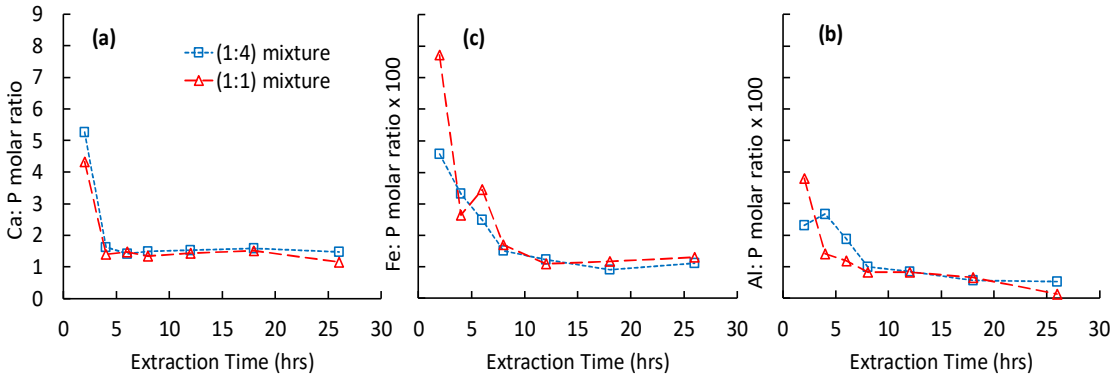


Figure 6.6 Relationship between solubilised P and Ca **(a)**, Fe **(b)** and Al **(c)** when DPR is cumulatively leached with pyrolysis condensate from maize stover pyrolysis.

Initially higher Fe:P molar ratios at 2 hours suggest significant dissolution from non-P associated Fe probably from gangue minerals in the DPR sample. However, subsequent leachates from 4 hours onwards had Fe:P ratios that were below the 0.059 value found in DPR (Figure 6.6b) but similar to when DPR was titrated with pure organic acids at pH 3 (Figure 6.2b).

Leachates from 2 hours to 6 hours had Al:P molar ratios that were higher than the 0.0097 value found in DPR (Figure 6.6c) indicating either some dissolution of non-P bound Al from gangue minerals, and/or preferential dissolution of Al over P from the apatite lattice. However, after 6 hours the Al:P ratio of leachates reduced to either the same, or below that of the Al:P molar ratio in the DPR, as more P was solubilised with less Al solubilised. This was not due to exhaustion of the Al content in the DPR, as less than 14% of the total

Al content was recovered after 26 hrs of sequential leaching using both pyrolysis liquid leaching ratios (Table 6.2).

6.4 Conclusions

Oxalic acid was more effective at solubilising total P from DPR, providing twice as much P in solution compared to citric acid at the same molar ratios, while maintaining the lowest Ca in solution. While three sequential extractions at pH 3 using lab grade oxalic and citric acids were able to solubilise a total of 46 and 22% P respectively, sequential leaching extractions with aqueous phase pyrolysis liquid over 26 hours solubilised less than 14% of the total P. Therefore, the use of pyrolysis condensate was relatively ineffective at solubilising total P from DPR. Further studies are recommended on pyrolysis conditions that might favour the production of higher oxalic acid titers, or low-cost processes that can be employed to produce oxalic acid in rural communities.

This chapter satisfies the thesis objective of evaluating the effectiveness of diluted pyrolysis condensate in solubilising agronomic P from DPR.

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CHAPTER 7

PHOSPHORUS UPTAKE BY RYEGRASS AND BROCCOLI FROM SLOW RELEASE GLASS SINTERED AND BIOCHAR FERTILISERS

In chapters 4 and 5, potential P fertilisers were developed and indexed for potential P-supply using common laboratory extraction methods. This chapter focusses on ascertaining whether the previously observed significant improvements in P reactivity of these modified Dorowa PR products, translated to significant improvements in P-supply to growing crops under the effect of soil conditions and type of plant (ryegrass and broccoli).

Glasshouse trial setup, 4 days after the 1st ryegrass harvest

Abstract

The use of alternative and innovative phosphorus (P) sources that utilise locally accessible and low-cost materials may offer a solution to smallholder resource-constrained farmers. In this study, newly developed P fertilisers were assessed for agronomic effectiveness under glasshouse conditions using broccoli and ryegrass as test crops. Sources of P consisted of Dorowa phosphate rock (DPR), DPR co-pyrolysed with biochar (DPR-B), DPR sintered with recycled glass at two mixing ratios (DPR-G1 and DPR-G2), DPR sintered with serpentine (DPR-S), a commercially available direct application phosphate rock (CDAPR) applied at rates of 60 and 120 mg citric soluble (citsol) P/ kg soil, and multiple rates of a standard monocalcium phosphate (MCP). All P sources resulted in a 2.5 to 5.3-fold increase in cumulative ryegrass shoot biomass compared to the unfertilised control. After 6 harvests, ryegrass that had DPR-B or DPR-G1 fertiliser applied had similar P uptake and produced at least 95% of the biomass produced when MCP was applied. A similar trend was observed under broccoli cropping where application of DPR-B or DPR-G1 fertilisers produced biomass yields and P uptake that was either comparable or higher than when MCP was applied. Results suggest that citsol P was a better estimator of bio-available P under ryegrass and cropping for the DPRB and DPR-G1 fertilisers, but not for DPRS. Initial economic analysis based on fertiliser substitution ratios under broccoli cropping, incorporating manufacture and transportation costs, revealed that the use of DPR-B or DPR-G1 as a P fertiliser product may result in savings of about 57 or 39% compared to using single super phosphate (SSP), respectively. These savings would provide a reasonable option for smallholder farmers around the Dorowa area in Zimbabwe where phosphate rock is mined. Repeated field studies with DPR-G1 and DPR-B are recommended with grasses, brassica crops, and maize. In addition, field studies should further investigate the ability of brassicas to use DPR as a P source.

7.1 Introduction

Soil phosphorus (P) deficiencies are common in tropical farming systems (Barreto *et al.*, 2018; Chikowo *et al.*, 2009; Gemenet *et al.*, 2015). In southern African smallholder farming areas, the unavailability and high cost of water-soluble fertilisers limit their use. Phosphorus use efficiency is also very low because most of the soils are P fixing, inherently acidic, infertile, and contain very little organic matter, (Nyamangara *et al.*, 2020). Accordingly, farmers apply insufficient fertiliser for crop production, leading to an estimated soil P depletion of between 1 to 6 kg of P ha^{-1} annually (Mafongoya *et al.*, 2006). Alternative and innovative P sources that utilise locally accessible and low-cost materials may provide a better option for resource-constrained farmers than imported, high cost, acidulated fertilisers. Direct application of phosphate rocks (PR) have been suggested as low-cost alternatives. However, most PRs in southern Africa are igneous, non-reactive, and have very little agronomic value in their unmodified state (Ajiboye *et al.*, 2018).

The more reactive PRs (of sedimentary and/or guano origin with < 30% citric acid soluble (citsol) P have been extensively studied as P sources for direct application (Rajan and Chien, 2003, Zapata and Roy, 2004), whereas research focusing on non-reactive igneous rocks has been limited. Techniques to improve the agronomic value of PRs such as co-treatment with elemental sulphur (ES) (Matamwa *et al.*, 2018) or triple super phosphate (TSP) (Chien, 2019; Soma *et al.*, 2017), calcination with K_2CO_3 (Nakamura *et al.*, 2019), and grinding to nanoparticles (Abd El-Halim and Omae, 2019), are reported in the literature. However, these resource or energy-rich techniques are not suitable for impoverished farmers on poor quality soils. For instance, grinding at the nanoscale is expensive (Abd El-Halim and Omae, 2019) and the cost of ES is high since it is imported.

In addition, moisture is needed for the dissolution of elemental S by *Thiobacillus* spp in soil, a condition which makes co-treatment with S unsuitable for dryland agriculture due to lack of effectiveness (Evans *et al.*, 2006). Where co-treatment with S has been reported as highly effective at increasing agronomic value, the host PR has been reactive in nature, such as Sechura PR (Evans *et al.*, 2006) and Minjingu PR (Matamwa *et al.*, 2018). When co-treating PRs with water soluble fertilisers such as TSP, a 50:50 (TSP/PR) mixing ratio has been recommended (Chien, 2019). This is still cost-prohibitive for smallholder farmers because water soluble P fertiliser prices in sub-Saharan Africa (SSA) are higher than the average global prices (Nakamura *et al.*, 2019), partly due to long transport distances with high costs. P fertilisers that can be made from local PR resources, either by thermal modification of low reactivity PR combined with silicates (Tumbure *et al.*, 2020b), or by co-pyrolysis of PR with waste plant residues (biochar) (Tumbure *et al.*, 2020a), can avoid high transport costs and thus be more cost effective. Fertilisers developed with these technologies remain to be tested for agronomic effectiveness.

Dorowa PR (DPR), the only commercially available PR in Zimbabwe, is igneous, composed of 89% hydroxy-fluorapatite ($Ca_5(PO_4)_3OH$ F) and 3.5% calcite ($CaCO_3$), and has very low reactivity (Tumbure *et al.*, 2019). Potential processes for creating a DPR product with improved P solubility through co-pyrolysis with maize stover, or thermal treatment with recycled glass at sub-fusion temperature ranges (< 1000 ^{o}C, ideal for use in traditional brick-firing kilns) have been previously explored (Tumbure *et al.*, 2020a; Tumbure *et al.*, 2020b). Heating DPR + glass mixtures at 900 ^{o}C was shown to improve citsol P by up to 73% compared to the unamended DPR (Tumbure *et al.*, 2020b). Another study, where a biochar-based P fertiliser (BBF) was produced from co-pyrolysis of the DPR with maize stover, increased citsol P by about 30% compared to the unamended

DPR (Tumbure *et al.*, 2020a). BBFs produced by co-pyrolysis usually have increased liming ability, with the associated cation exchange and water retention capacities potentially providing multiple benefits to the acidic, sandy and infertile soils in southern Zimbabwe (Tumbure *et al.*, 2020a; Gwenzi *et al.*, 2017).

The objective of the present study was to evaluate biochar-based, glass-sintered and serpentine-sintered P sources on biomass production and P uptake of annual ryegrass (*Lolium multiflorum* Lam.) and broccoli (*Brassica oleracea* var. italica) in a weathered sand under glasshouse conditions. This allowed testing of the effect of interactions between the fertilisers, the weathered sand and plant characteristics on agronomic effectiveness (Ahmad *et al.*, 2019; Chikowo *et al.*, 2009; Kafesu *et al.*, 2018; Fukuda *et al.*, 2013).

7.2 Materials and methods

7.2.1 Rooting media

The soil for rooting media was collected as a subsoil from an Otangaroa loamy sand soil, (NZ soil classification order: Recent Sandy), in Limestone Downs, New Zealand (37°30'39.61" S; 174°44'51.37"). This weathered coastal sandy subsoil was selected to be the closest low available-P analogue to the local Zimbabwean soil where the fertiliser products may potentially be used. The subsoil was air dried then sieved through a 2 mm sieve, and a sample for characterisation was obtained by coning and quartering. The subsoil was analysed for available P using the molybdenum blue method, after extraction in 0.5M $NaHCO_3$ (Olsen, 1954). Exchangeable bases were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) after extraction in 1M neutral ammonium acetate and soil pH was measured potentiometrically in a 1:2 (v/v) soil/ water slurry. Anion retention was analysed after equilibration of 5 g the subsoil with a 1000 mg/

L P solution (Saunders, 1965). Soil analysis revealed that the soil had high levels of Na^+ compared to soils where the potential fertilisers may be used. (Table 7.1). Accordingly, all pots (containing 1.5 kg subsoil) were leached with 5.6 L of water by applying 0.7 L of tap water 7 times and letting it drain free to remove excess Na^+. An 8th leaching was performed with de-ionised water. After leaching, the Na^+ content of the subsoil had reduced at least 3-fold from 2.4 to 0.7 $cmol_c\ kg^{-1}$ subsoil. The subsoil had a bulk density of 1.2 g cm^{-3} when packed into pots, moisture contents of 32% at water field capacity (at -0.1 bar), 15% at water stress point (at -1 bar), and 13% at water permanent wilting point (at -15 bar).

Table 7.1 Initial chemical characteristics of the subsoil and the leached subsoil used as rooting media

	pH	**Olsen P (mg kg^{-1})**	**Anion retention (%)**	**Total base sat (%)**	**Ca sat (%)**	**Mg sat (%)**	**Na sat (%)**	**K sat (%)**	**CEC (cmol $_c\ kg^{-1}$)**	**Exchangeable bases (cmol $_c\ kg^{-1}$)**			
										K	**Ca**	**Mg**	**Na**
1*	6.5 ± 0.1	7.0 ± 0.0	26 ± 1.5	83.7 ± 1.9	26.3 ± 0.3	35.3 ± 1.1	20.7 ± 0.7	1.5 ± 0.1	12 ± 0.0	0.18 ± 0.01	3.10 ± 0.00	4.17 ± 0.08	2.45 ± 0.06
2*	7.3 ± 0.2	6.3 ± 0.3	26.0 ± 1.5	83.3 ± 0.7	33.7 ± 0.3	40.5 ± 0.4	7.5 ± 0.1	1.9 ± 0.0	8.7 ± 0.3	0.17 ± 0.01	2.93 ± 0.07	3.57 ± 0.08	0.66 ± 0.03

*1 – pre-leaching, 2 – post leaching, numbers after ± are standard error of means (n=3), sat - saturation

7.2.2 Experimental setup.

Two independent sets of experiments, using either ryegrass (*Lolium multiflorum* Lam.) or broccoli (*Brassica oleracea* var. italica) as the test plants, were conducted. Ryegrass was used as a test crop because its growth pattern allowed multiple harvests, and many researchers have used it to evaluate P fertilisers (Wang *et al.*, 2014). Broccoli was selected as a second test crop because leafy brassica spp such as broccoli and kale are grown widely all year round in Zimbabwe serving local markets as a staple relish (Nyamupingidza and Machakaire, 2003; Wulff *et al.*, 2002). Broccoli also serves export markets such as the United Kingdom (Dolan and Humphrey, 2000), significantly

contributing to family incomes. Brassicas have the largest land area contribution to the cultivated Cruciferae family in eastern and southern Africa (Varela *et al.*, 2003). Treatments consisted of seven types of P fertilisers (Table 7.2) applied at rates of 60 and 120 mg of citsol P kg^{-1} of subsoil giving a 7 x 2 factorial experiment each for broccoli and ryegrass. Fertilisers were applied based on their citsol P content and not on a total P (TP) basis. The rationale being that citsol P content has been used as an index of agronomically effective P (Quin, 1985) and plant available P content in PRs (Mackay *et al.*, 1984), and in fertilisers containing partially soluble and soluble P (Condron *et al.*, 1994). Solubility in citric acid is an official method for testing fertiliser quality in Zimbabwe, New Zealand, and the European Union (EU, 2003; Fertmark, 2016). Adding potentially similar amounts of plant available P avoids P-deficient crop growth, which occurs when P sources deliver little plant available P and can thus compromise relative yield and fertiliser substitution rate assessments. For example, Govere *et al.* (2003) found that additions of DPR up to 150 mg TP kg^{-1} soil caused no significant increase in DM compared to an unfertilised control. A no-P control was included in the pot trials, with the monocalcium phosphate (MCP) treatment serving as a positive P control. All treatments were replicated four times and arranged in a randomised complete block design (RCBD). Additional pots with MCP were applied at rates of 60, 120, 180, 240, 300, 360, 420, and 480 mg citsol P kg^{-1} subsoil and replicated four times. These rates were selected to better define the plant growth response to P.

Production of the DPR-G, DPR-S, and DPR-B fertilisers used in this study are discussed in full elsewhere (Tumbure *et al.*, 2020a; Tumbure *et al.*, 2020b). Briefly, DPR-B was made by pyrolysing maize stover + DPR at 450 ^{o}C, and DPR-G was made by heating milled recycled glass + DPR at 900 ^{o}C. The TP and amount of citsol P for the various P sources used are shown in Table 7.2.

Table 7.2 Selected characteristics of fertiliser materials used.

Fertiliser type	Abbreviated name	Total P (%)	Citsol P (% of TP)	g fert/kg soil (mg total P/kg soil)	Main crystalline mineral constituents	Ref
DPR + soda glass (1:1)	DPR-G1	8.5	34.2	2.1 (175), 4.1 (351)	wollastonite, quartz, muscovite, hydroxy-fluorapatite (with some SiO_4 substitutions)	1
DPR + soda glass (1:2)	DPR-G2	5.6	39.1	2.7 (153), 5.5 (307)	wollastonite, quartz, muscovite, hydroxy-fluorapatite (with some SiO_4 substitutions)	1
DPR + serpentine (1:2)	DPR-S	6.0	41.5	2.4 (145), 4.8 (289)	fosterite, hieratite, hydroxy-fluorapatite (with some SiO_4 substitutions)	1
DPR	DPR	16.5	12.1	3.0 (496), 6.0 (992)	hydroxy-fluorapatite, calcite	2
Commercial direct application PR (30% Algerian PR + 70% Sechura PR)	CDAPR	12.9	26.1	1.8 (230), 3.6 (460)	calcite, carbonate substituted hydroxy-fluorapatite	4,5
DPR + maize biochar	DPR-B	5.6	33.6	3.2 (179), 6.4 (357)	Sylvite, calcite, hydroxy-fluorapatite (with some P-O-C bonding)	3
Mono calcium phosphate	MCP	25.4	100	0.2 (60), 0.5 (120)		

1 (Tumbure *et al.*, 2020b), 2(Tumbure *et al.*, 2019), 3 (Tumbure *et al.*, 2020a), 4 (Végh *et al.*, 2009), 5 (Mackay *et al.*, 1984)

The commercially available direct application phosphate rock (CDAPR) was a blend of 70% Sechura PR from Peru and 30% Algerian PR and was supplied by Ravensdown fertiliser co-operative ltd, New Zealand.

7.2.3 Planting and experimental management

Air-dried soil (1532 ±1 g, moisture 2.1%) was weighed into strong plastic bags. Phosphate fertilisers were applied as a basal dressing to the soil in each plastic bag and thoroughly mixed. The fertilised soil was transferred to a 2L pot (14.3 cm top internal diameter x 15 cm slopping height) equipped with a nylon mesh at the bottom. For the ryegrass experiment, ryegrass seeds were directly seeded into the pots at 40 seeds per pot. For the broccoli experiment, two broccoli seedlings (3-leaf stage, obtained from a commercial nursery) were transplanted into each pot. All pots were initially watered to field capacity (0.1 bar) using distilled water. Ryegrass was thinned to 20 plants per pot 15 days after planting (DAP). Broccoli transplanting was 100% successful and two plants remained in each pot. Soil water was checked once a day by weighing the pots and replenished with distilled water to 75% of field capacity. Phosphate-free nutrient solution was applied twice per week at 0.15 L per pot. The phosphate-free nutrient solution (Middleton and Toxopeus, 1973) contained the following nutrient compounds per litre; 27 g NH_4NO_3, 7.35 g K_2SO_4 (anhydrous), 2.22 g $MgSO_4.7H_2O$, 1.80 g $CaCO_3$ (anhydrous), 36 ml of 1M HCl, 3.29 g NaCl, 3.0 mg H_3BO_3, 1mg $CuCl_2.H_2O$, 20.0 mg $MnCl_2.H_2O$, 0.4 mg $(NH_4)Mo_7O_{24}.4H_2O$, and 1.5 mg $ZnCl_2$. The glasshouse temperature was set in the range 20 - 25 ^oC and the experiments were maintained for 141 and 68 days after planting/transplanting for ryegrass and broccoli, respectively. A timeline of operations, average day and night temperatures during the growth of broccoli and ryegrass (6 harvests) in the glasshouse are shown in Figure 7.1. During the experiments, average day and night temperatures ranged between 10 to 30 ^{o} C.

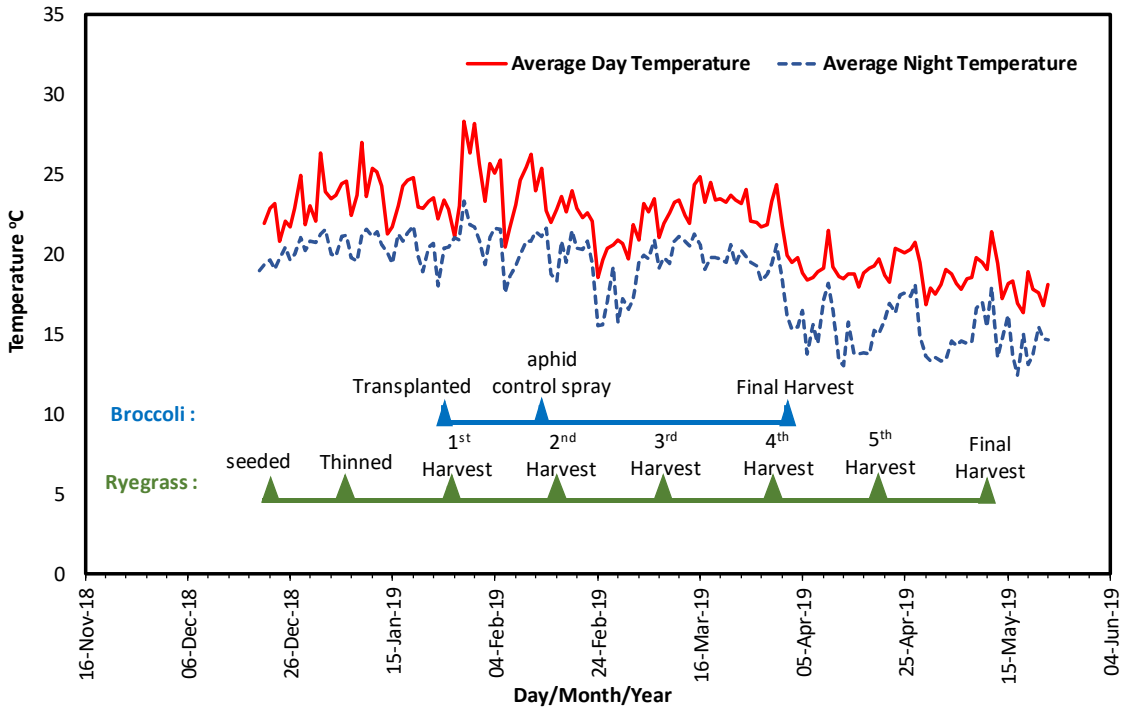

Figure 7.1 Average day and night temperatures during the glasshouse experiments and timeline of operations.

7.2.4 Data collection and analysis

Ryegrass was harvested every 2 - 4 weeks (depending on growth rates) by cutting shoots 5 cm above the ground and drying to a constant mass at 70 °C in an oven. A total of 6 ryegrass harvests were performed, and data are presented as a cumulative of the 6 harvests unless otherwise stated. Broccoli was harvested by cutting 3 cm above the ground, 68 days after transplanting, and before the broccoli had started to form florets. After weighing the dry biomass, the plant material was ground to < 1 mm using a Foss CT293 cyclotech^{TM} laboratory mill. Total P was determined colorimetrically on a Technicon autoanalyser after Kjeldahl digestion of ground herbage subsamples (McKenzie and Wallace, 1954). Other elemental analyses have not been reported because all plants were

grown with a P-free, complete nutrient solution, ensuring that other elements were not limiting. P uptake was calculated as **(7.1)**:

$$P\ uptake\ (mg\ kg^{-1}\ soil) = Drymass\ (mg\ kg^{-1}\ soil)\ \times\ P\ content\ (\%) \qquad (\mathbf{7.1})$$

To compare the effectiveness of the various P sources in supplying plant available P, apparent P recovery rate (PRR) of the citsol fraction was calculated according to equation (7.2):

$$PRR\ (\%) = \left[\frac{P\ Uptake_{treatment} - P\ Uptake_{No\ P\ control}}{Citric\ soluble\ P\ applied}\right] \times 100 \qquad (\mathbf{7.2})$$

The biomass yield responses versus applied citsol P for both ryegrass and broccoli, when MCP was applied, were fitted to a Mitscherlich equation, written as (Wang *et al.*, 2014) (7.3):

$$Y = Y_o + \Delta Y - \Delta Y e^{-\varepsilon N f} \qquad (\mathbf{7.3})$$

Where Y is total dry matter or P uptake, Y_o is yield or P uptake without fertiliser, ΔY is the difference between maximum yield/P uptake and Y_o, ε is a response constant, and Nf is the rate of fertiliser applied (citsol P). This fitted equation (obtained using MCP biomass yield) was used to quantify the variance in biomass or P uptake observed with test fertilisers, by calculating the determination coefficient (R^2) as (7.4);

$$R^2 = 1 - \frac{\sum\left(Y - \acute{Y}\right)^2}{\sum(Y - \bar{Y})^2} \qquad (\mathbf{7.4})$$

Where Y is the observed biomass/P uptake produced by test fertilisers, $\acute{Y}$ is the MCP predicted value from the Mitscherlich equation, and $\bar{Y}$ is average of observed values from test fertilisers.

The Mitscherlich equation was then used to estimate the MCP rate required to achieve the same biomass yields as the other P treatments, and this was expressed as the fertiliser substitution ratio (SR), calculated according to equation (7.5) as follows:

$$SR = \frac{MCP\ rate\ citric\ sol.P}{Treatment\ rate\ citric\ sol.P} \qquad (\mathbf{7.5})$$

SR represents the fractional rate of MCP that is required to generate the same biomass yield as a fertiliser treatment applied at 60 or 120 mg citsol P kg^{-1} soil.

Comparisons of intrinsic P use efficiency differences, between ryegrass and broccoli, were calculated as the physiological efficiency (*PE*) according to equation (7.6):

$$PE\ (g\ biomass\ mgP^{-1}) = \frac{Biomass_{Treatment} - Biomass_{No\ P\ control}}{P\ Uptake_{Treatment} - P\ Uptake_{No\ P\ control}} \qquad (\mathbf{7.6})$$

An analysis of variance of shoot biomass and P uptake was conducted using a two-way model to test the fixed effect of P source, the level of citric soluble P applied, and the interaction of P source and citric soluble P applied, after checks of normality and equal variance were performed. If a significant ($P < 0.05$) effect was detected, then the difference between treatment means was tested using least significant difference (LSD).

7.3 Results

7.3.1 Ryegrass biomass yield and P uptake

Compared to the unfertilised control (No P), all added P sources resulted in a 2.5 to 5.3-fold increase in cumulative ryegrass shoot biomass (Figure 7.2a). The type of P source and the rate applied, significantly ($P < 0.001$) affected biomass production of ryegrass.

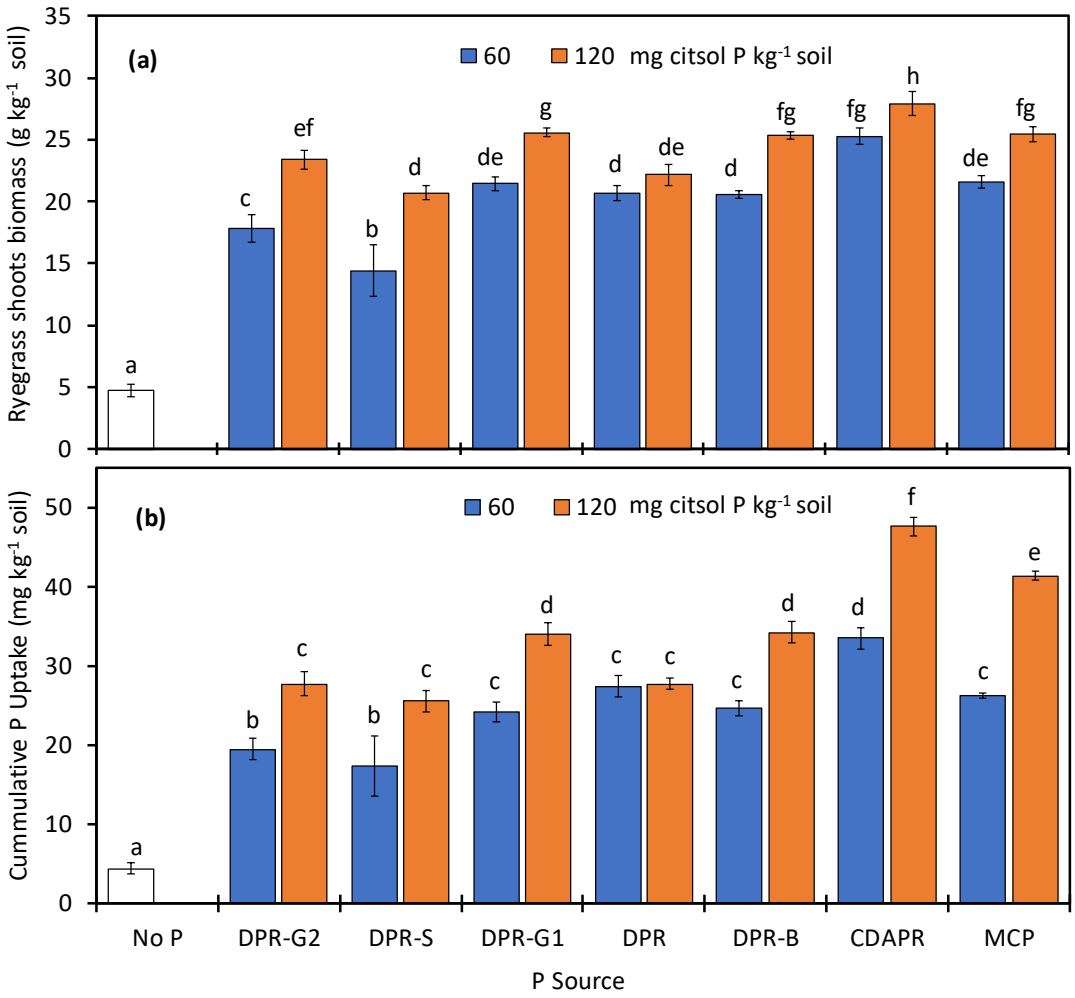

Figure 7.2 Cumulative (a) biomass yield and (b) P uptake of ryegrass after the 6th harvest. Error bars indicate 2x standard errors of means (n = 4) and columns with the same letter are not significantly different from each other.

The interaction between P source and rate was also significant ($P = 0.013$). At 60 mg citsol P kg^{-1} application rate, the cumulative biomass of the MCP treatment was similar

to that of the DPR-G1, DPR-B, and DPR treatments. Increasing the rate of citsol P applied from 60 to 120 mg P kg^{-1} significantly increased ($P < 0.001$) cumulative ryegrass biomass for all other treatments, except for the DPR treatment. At both citsol P application rates, the DPR-G1, DPR-B, and CDAPR treatments produced at least 95% of the biomass of MCP treatment. The DPR-G2, DPR-S, and DPR treatments produced 82, 67, and 96% of the MCP biomass yield, respectively, when applied at 60 mg P kg^{-1} soil.

The Mitscherlich equation explained 99% of the variation in ryegrass growth responses to increasing rates of citsol P applied as MCP (Figure 7.3). The growth responsive region was between rates of 0 to 210 mg citsol P kg^{-1} soil.

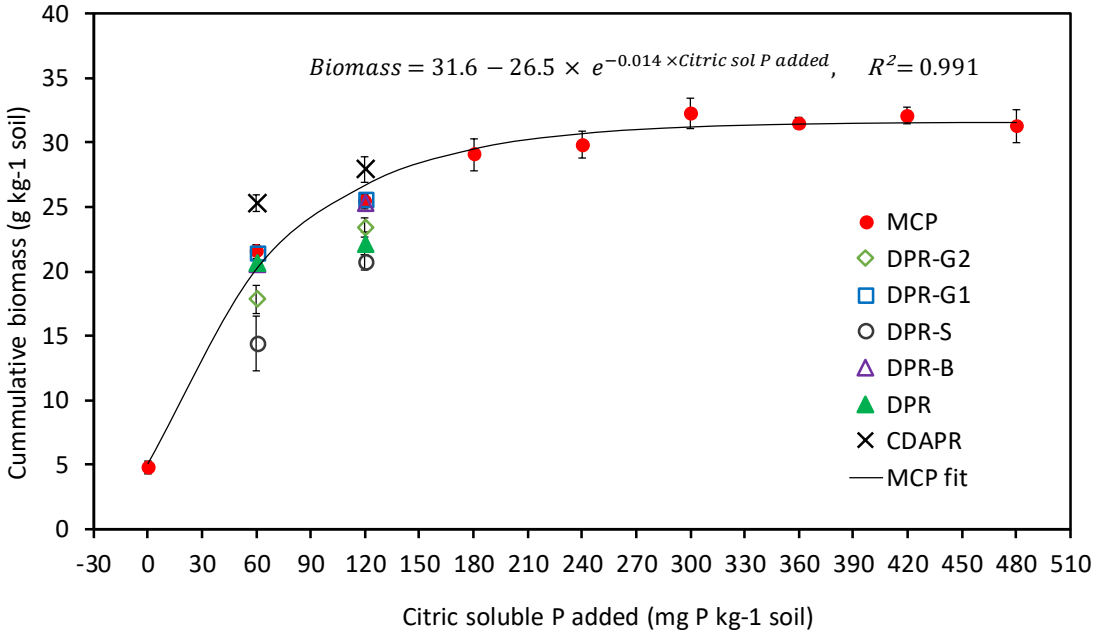

Figure 7.3 Ryegrass cumulative biomass response to P addition as fitted by a Mitscherlich equation. Error bars indicate 2x standard error of means (n=4).

Ninety five percent of ryegrass maximum yield (30 g kg^{-1} soil) was achieved with an MCP rate of 200 mg citsol P kg^{-1} soil. The yields produced by DPR-G1 and DPR-B, both

at 60 and 120 mg citsol P kg^{-1}, were not significantly different to the fitted MCP equation, which explained 72% of the variation in ryegrass shoot biomass grown with the DPR-G1 and DPR-B fertilisers. At the rate of 60 mg citsol P kg^{-1} soil, the CDAPR treatment produced biomass that was above the fitted responsive curve (Figure 7.3).

Ryegrass herbage P concentrations ranged from 0.07 to 0.30% P for the P sources at each harvest (Appendix 2: Table S7.1). The cumulative P uptake of ryegrass after 6 harvests in the unfertilised control was very low at 4.8 mg P kg^{-1} soil and ranged between 18 and 47 mg P kg^{-1} soil for the fertilised soil. Phosphorus uptake increased with application rate in all other treatments except for the DPR treatment. (Figure 7.2b). When applied at 60 mg citsol P kg^{-1} soil, the DPR, DPR-G1, DPR-B, and CDAPR treatments had P uptake that was at least 92 % of the MCP treatment. Cumulative P uptake in the DPR-G1, DPR, and DPR-B treatments was not significantly different to that of the MCP treatment when applied at 60 mg citsol P kg^{-1} soil (Figure 2b). There was also a strong linear correlation (R^2 = 0.998) between ryegrass P uptake and citsol P applied as MCP (Appendix 2: Figure S7.1).

By the final harvest, the apparent P recovery (% PRR) by ryegrass, when MCP was applied at 60 mg citsol P kg^{-1} soil was 36% (Table 7.3). At the same application rate, % PRR values for the other P sources were in the order DPRS < DPR-G2 < DPR-G1 = DPR-B < DPR < CDAPR and ranged between 15 to 48%. At the higher application rate of 120 mg P kg^{-1} soil, the ryegrass % PRR values were lower for all the P sources (Table 7.3).

Table 7.3 Cumulative apparent P recovery rate (PRR) and fertiliser substitution ratios (SR) of ryegrass when fertilised with various P sources.

Treatment	When 60 mg citsol P kg^{-1} soil was applied						When 120 mg citsol P kg^{-1} soil was applied					
Apparent P Recovery Rate (%)												
Cumulative Harvest	**1**	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**	**5**	**6**
DPR-S	0.12 ± 0.12	2.78 ± 0.39	6.79 ± 0.63	10.26 ± 1.91	12.86 ± 2.53	15.34 ± 2.86	0.18 ± 0.10	3.97 ± 0.63	8.69 ± 0.39	12.56 ± 0.55	15.20 ± 0.81	17.63 ± 1.09
DPR-G1	2.58 ± 0.14	9.46 ± 0.55	16.80 ± 1.23	23.07 ± 1.83	27.91 ± 1.96	33.02 ± 2.12	3.83 ± 0.27	9.01 ± 0.32	14.43 ± 0.47	18.77 ± 0.74	22.04 ± 1.01	24.74 ± 1.19
DPR-G2	1.36 ± 0.61	6.57 ± 1.02	12.91 ± 0.74	18.82 ± 0.63	23.12 ± 1.11	26.91 ± 1.86	2.49 ± 1.01	6.57 ± 1.10	10.95 ± 1.14	14.40 ± 1.08	16.97 ± 1.10	19.45 ± 1.26
DPR-B	0.53 ± 0.19	7.13 ± 0.96	15.81 ± 0.98	23.92 ± 1.23	29.14 ± 1.50	33.82 ± 1.54	2.02 ± 0.39	6.74 ± 0.37	12.22 ± 0.51	17.51 ± 0.83	21.22 ± 1.02	24.87 ± 1.12
DPR	0.06 ± 0.03	4.97 ± 0.32	15.06 ± 0.99	25.11 ± 0.65	32.54 ± 1.23	38.34 ± 2.32	0.02 ± 0.02	4.42 ± 1.28	9.39 ± 1.29	13.82 ± 0.79	16.94 ± 0.52	19.45 ± 0.65
CDAPR	2.56 ± 0.29	10.60 ± 0.69	20.54 ± 0.95	30.32 ± 0.90	39.93 ± 1.36	48.45 ± 2.15	2.17 ± 0.10	8.03 ± 0.12	15.89 ± 0.50	23.44 ± 0.80	30.80 ± 0.80	36.04 ± 1.00
MCP	6.27 ± 0.40	15.35 ± 0.21	22.49 ± 0.32	27.79 ± 0.24	31.83 ± 0.32	36.39 ± 0.48	6.13 ± 1.00	14.64 ± 0.84	21.64 ± 0.76	25.90 ± 0.72	28.46 ± 0.54	30.81 ± 0.49
Substitution Ratios												
DPR-S	-	0.11	0.23	0.37	0.47	0.51	-	0.12	0.27	0.40	0.49	0.53
DPR-G1	-	0.50	0.72	0.90	1.06	1.14	-	0.43	0.61	0.74	0.84	0.88
DPR-G2	-	0.33	0.51	0.64	0.75	0.78	-	0.29	0.46	0.58	0.65	0.70
DPR-B	-	0.26	0.52	0.80	0.98	1.04	-	0.32	0.52	0.70	0.80	0.85
DPR	-	0.12	0.38	0.71	0.96	1.05	-	0.11	0.27	0.45	0.57	0.61
CDAPR	-	0.51	0.85	1.20	1.54	1.70	-	0.34	0.61	0.85	1.08	1.17
MCP	-	1.00	1.00	1.00	1.00	1.00	-	1.00	1.00	1.00	1.00	1.00

Notably, the % PRR values for the CDAPR and DPR sources exceeded those of the MCP standard, indicating a greater amount of P was released to ryegrass than indicated by their citsol P content. All other sources, however, had lower % PRR values, than MCP, indicating that they released a lower amount of plant available P than indicated by their citsol P content. The DPR-G1 and DPR-B treatments delivered % PRR values that were much closer to that of the MCP (< 9% difference). Promisingly, the cumulative yield after the 6th harvest, indicated that CDAPR, DPR-G1, and DPR-B, had MCP fertiliser SR's of 1.7, 1.1 and 1.0, respectively, indicating that they were as agronomically effective as the MCP or better when applied at the same citsol application rates.

7.3.3 Broccoli biomass yield and P uptake

Biomass yield of broccoli from the DPR-S, DPR-G1, DPR, DPR-B, CDAPR, and MCP treatments were not significantly different from each other at 60 mg citsol P kg^{-1} soil application rates (Figure 7.4a), indicating a low sensitivity to P source. The DPR-G2 treatment produced the lowest broccoli biomass of all the P sources applied at 60 mg citsol P kg^{-1} soil. A fitted Mitscherlich equation explained 98% of the variation in broccoli yield response to increasing amounts of citsol P applied as MCP and indicated that the growth response region for broccoli was between 0 to 150 mg citsol P kg^{-1} soil (Figure 7.5). Ninety five percent of the maximum broccoli yield (23 g kg^{-1} soil) was achieved with an MCP rate of 102 mg citsol P kg^{-1} soil. However, the Mitscherlich equation fitted to the MCP biomass responses could not explain a significant amount of the variation in the yield response of broccoli to the other P fertilisers.

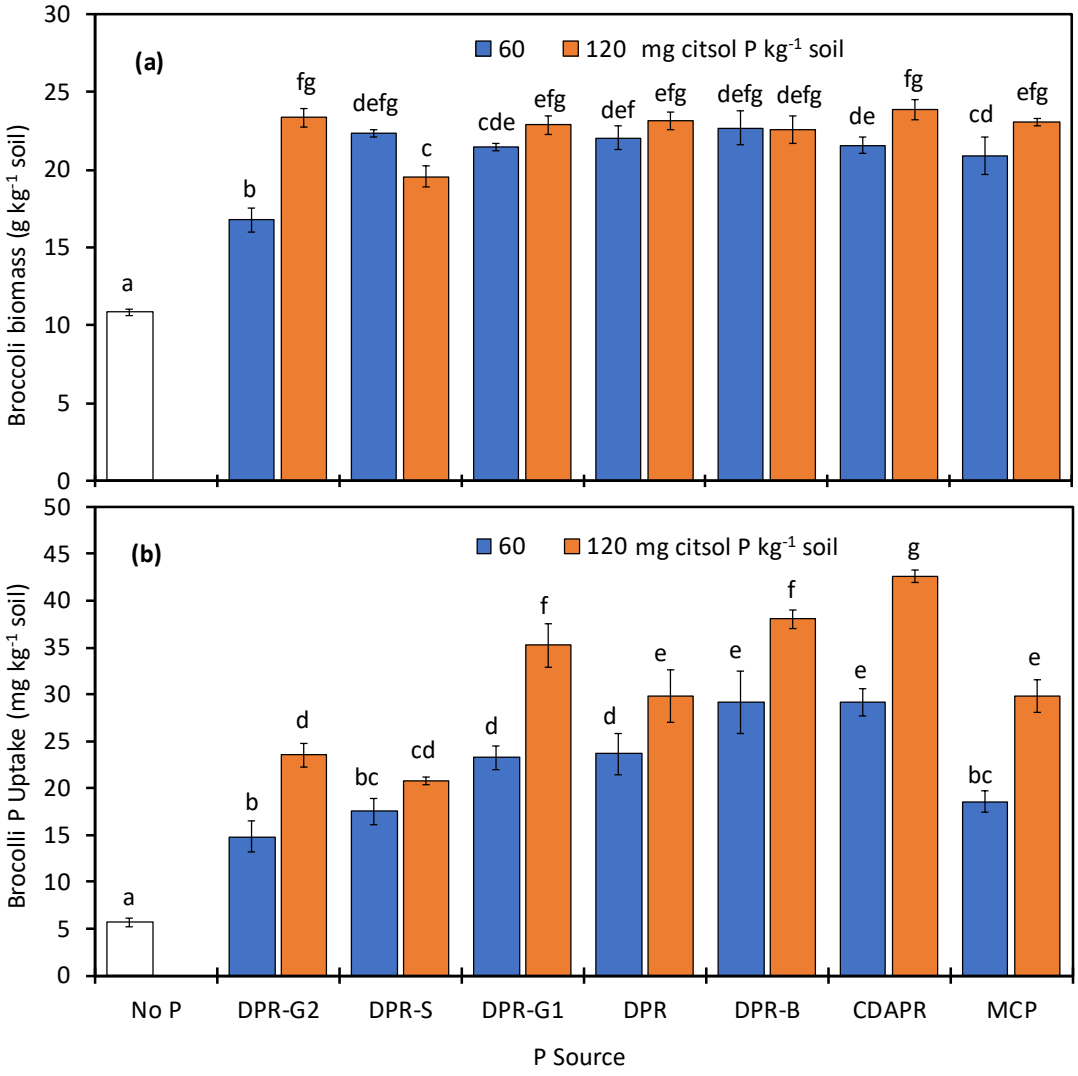

Figure 7.4 (a) Biomass yield and **(b)** P uptake of broccoli 68 days after transplanting. Error bars indicate 2x standard errors of means (n = 4) and columns with the same letter are not significantly different from each other.

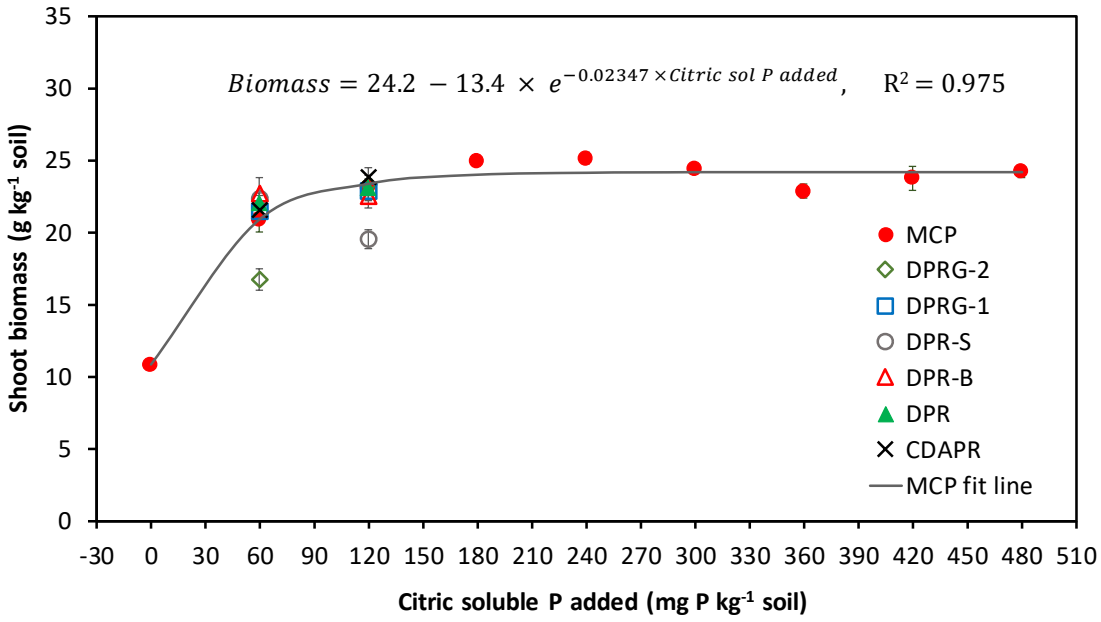

Figure 7.5 Biomass response to P addition of broccoli as fitted by a Mitscherlich equation. Error bars indicate 2x standard error of means (n=4).

The yields produced by all P sources (except for DPR-G2) applied at 60 mg citsol P kg^{-1} soil, and DPR-S applied at 120 mg citsol P kg^{-1} soil, were either the same as, or above the MCP fitted curve. The DPR-G1, DPR, CDAPR, and DPR-B treatments produced biomass yields that were between 89 to 98% of the maximum biomass yield at both P application rates.

The % P values of broccoli shoots ranged from 0.09 to 0.19% for the tested P sources (Appendix 2: Table S7.2). The broccoli P uptake response, and the amount of citric soluble P applied for the MCP treatment, was fitted to a Mitscherlich equation (R^2 = 0.986) giving the maximum P uptake in broccoli shoots at 91.7 mg P kg^{-1} soil (Appendix 2: Figure S7.2). As shown in Figures 7.5 and S7.2, an increase in P uptake with application rate from 180 to 480 mg citsol P kg^{-1} occurred when biomass production had

plateaued, resulting from increased P content at these high application levels. The unfertilised control (no P) had a P uptake of 5.7 mg P kg^{-1} soil and ranged between 12 and 42 mg P kg^{-1} soil for the fertilised soil at 60 and 120 mg citsol P kg^{-1} soil. Increasing the P application rate led to significantly greater ($P < 0.01$) P uptake in all the P fertiliser treatments except for the DPR-S treatment (Figure 7.4b). At 60 and 120 mg citsol P kg^{-1} soil application rates, the DPR-G1, DPR-B, DPR, and CDAPR treatments had P uptake, and therefore % PRR values (Table 7.4), that were significantly higher than that of the MCP treatment. When applied at 60 mg citsol P kg^{-1} soil, the DPR-G1, DPR-B, DPR, and CDAPR treatments had SRs that ranged from 1.1 to 1.5.

Table 7.4 Apparent P recovery rate (PRR) and fertiliser substitution ratios (SR) of broccoli 68 days after transplanting

Treatment	60 mg citsol P kg^{-1} soil		120 mg citsol P kg^{-1} soil	
	PRR (%)	SR	PRR (%)	SR
DPR-S	19.78 ± 2.39	1.39	12.59 ± 0.36	0.38
DPR-G1	29.36 ± 2.12	1.12	24.62 ± 1.98	0.82
DPR-G2	15.27 ± 2.71	0.42	14.87 ± 1.03	1.41
DPR-B	39.13 ± 5.56	1.54	26.94 ± 0.86	0.74
DPR	29.97 ± 3.70	1.29	20.12 ± 2.28	0.89
CDAPR	39.10 ± 2.49	1.15	30.77 ± 0.57	1.25
MCP	21.50 ± 1.94	1.00	20.07 ± 1.44	1.00

Numbers after ± are standard error of means

7.3.4 Physiological efficiency differences between ryegrass and broccoli

The six ryegrass harvests produced dry matter yields ranging from 14.4 to 27.9 g kg^{-1} soil, whereas the single broccoli harvest produced a range of 16.8 to 24 g kg^{-1} soil. Additionally, the slightly higher herbage P content for ryegrass resulted in higher PRR values for the six accumulated ryegrass harvests than for the single broccoli harvest. Notably, the physiological efficiency (PE) values (g biomass mg P^{-1}) for ryegrass (six

cumulative harvests) at all rates of P fertilisers, ranged from 0.54 to 0.87 and were generally higher than those for broccoli (ranging from 0.35 to 0.97) (Appendix 2: Table S7.3).

7.4 Discussion

7.4.1 P solubility and agronomic effectiveness of the DPR-based fertilisers

Applying the test fertiliser sources on an equivalent citsol P basis resulted in plant vigour being maintained in all treatments. This overcame the problem of poor plant growth due to lack of plant available P added, confounding evaluation of the fertiliser source. In New Zealand, the citric acid solubility of single superphosphate (Quin, 1985) and sparingly soluble P sources is recommended to guide the rates of effective P application in the field. The unmodified sample of DPR had less than 13% of TP soluble in 2% citric acid, similar to other low solubility igneous phosphate rocks (Leon et al., 1986). At 16.5% TP, 3 g of DPR was therefore required to supply 60 mg of citsol P kg^{-1} soil. The grade of MCP used in this experiment is 100% soluble in 2% citric acid. The substitution ratio, calculated from a comparison of the cumulative biomass yields of ryegrass produced at the end of 6 harvests on soil fertilised with MCP and DPR (Figure 7.3 and Table 7.3), indicated that the 3 g (60 mg citsol P) of applied DPR behaved as if it contained 63 mg of citsol P. Applied at a rate of 120 mg citsol P kg^{-1} soil, the DPR behaved as if it contained only 73 mg of citsol P. Calculations for the fertilisers using broccoli as a test plant gave a different result. At application rates of 60 and 120 mg citsol P kg^{-1} soil, DRP behaved as if it contained 77 mg and 107 mg of citsol P kg^{-1} soil, respectively (Figure 7.5, Table 7.4).

The Mitscherlich model for ryegrass (MCP, response curve, Figure 3) could not explain a significant percentage of the variance in cumulative ryegrass growth response for all

the P sources pooled together. However, for the DPR-G1 and DPR-B fertilisers, the predictive power of the model improved, with a coefficient of determination (R^2) of 72%. However, under broccoli cropping, the MCP Mitscherlich model (Figure 5) could not explain a significant percentage of the variance in the broccoli growth response to the P sources. Most P sources produced broccoli biomass that was above the model's maximum biomass value.

There is agreement with Kratz *et al.* (2019), that citsol P is not a universal measure of the agronomic effectiveness of P fertilisers since actual dissolution of PRs and its products in the soil environment is influenced by numerous soil properties. However, laboratory extractions such as citsol P are still important as reasonable estimates of P source quality that is used to guide application rates. Secondly, the agronomic effectiveness of P fertilisers is dependent upon the test plant's physiological efficiency and the plant/soil interaction, expressed as apparent P recovery. It is worth noting that when maize was used as a test plant in an acidic and P-deficient soil, Govere *et al.* (2003) was unable to show any significant agronomic value for DPR application. The same authors reported similar results when ryegrass was used as a test crop with DPR (Govere *et al.*, 2005). Kratz *et al.* (2019) highlight that unexplained variance can result from overestimation of bioavailable P by using citsol P, because of the relatively high solubility of apatites in citric acid. Another contribution to observed unexplained variance could be restricted growth due to physical limits in a pot trial causing a levelling-out of potential fertiliser-induced biomass differences. For ryegrass and broccoli growing on soil fertilised with CDAPR in the present study, the citsol P underestimated bio-available P. This is likely due to the fact that both Sechura and the Algerian PRs contain about 9% and 18% $CaCO_3$, respectively (Végh *et al.*, 2009; Mackay *et al.*, 1984; Bolan and Hedley, 1989), which would neutralise

some acidity in the 2% citric acid, and therefore give lower citsol P values (Mackay *et al.*, 1984).

7.4.2 P uptake and recovery rate from the various P sources

The response of cumulative ryegrass P uptake after the 6th harvest was linearly related to the MCP applied (Appendix 2: Figure S7.1), even at citsol P levels where biomass had reached a plateau (Figure 7.3). The linear model (Appendix 2: Figure S7.1) could not explain a significant percentage of the variance in cumulative ryegrass P uptake responses for all the P sources pooled together. The ryegrass herbage P concentration obtained in this study was similar to ryegrass herbage P concentrations reported by (Cheuyglintase *et al.*, 2018) of 0.05 to 0.20% P when MCP was applied up to 240 mg P kg^{-1} soil in a silt loam soil with low available P. The slow release nature of the test P sources is evident from the PRR curve along the harvest sequence (Table 7.3), indicating that the P source and soil interaction limited P uptake.

Broccoli P uptake and citsol P applied could be fitted to a Mitscherlich equation (Appendix 2: Figure S7.2), showing reduced marginal increases in P uptake as the amount of citsol P was increased beyond where biomass had reached a plateau (Figure 7.5). The fitted Mitscherlich equation explained only 11% of the variance in P uptake by broccoli shoots for all tested fertilisers, and 25% of the variance when only DPR-G1 and DPR-B fertilisers are considered. The % P values of broccoli shoots with test fertilisers (0.09 to 0.18 % P, Appendix 2: Table S7.2) were within range of those reported by Peralta-Antonio *et al.* (2019) of 0.15 and 0.19% P when broccoli was unfertilised and fertilised with 350 kg P ha^{-1}, respectively.

For all the P sources tested, except for MCP and DPR-S at 60 mg citsol P kg^{-1} soil, ryegrass after the 6^{th} harvest exhibited greater physiological efficiency than broccoli. It is likely that biomass production of broccoli was restricted by the size of pots, resulting in more P uptake that did not convert to biomass, or, at the time of harvest, P in above-ground tissue had not yet had time to be converted to biomass. Kratz *et al.* (2019) explains that the stage at which biomass is harvested can have a quite significant effect on the biomass vs P uptake relationship. The gradual increase in physiological efficiency with each succeeding ryegrass harvest suggests that the initial P extractive processes by the plant (which include root growth and rhizosphere modifications) happen at the expense of above-ground biomass production.

Compared to ryegrass that was added as seed to the pots, transplanting the broccoli with seedling P reserves and developed roots is likely to have enabled the plants early access to effective P uptake from the various P sources. Analysis of the seedlings (data not shown) revealed that the seedings had an average dry mass of 0.17 g per plant and a high P content of 0.6%, adding about 0.67mg P kg^{-1} soil. The high P content in broccoli seedlings at transplanting is likely to have circumvented initial P deficiency in plants grown with the slow P-release fertilisers.

Other researchers have reported brassica cultivars to be tolerant of P deficiency stress by creating a better rooting system through translocating absorbed P from metabolically inactive leaves to active roots (Akhtar *et al.*, 2007). Broccoli also employs the same mechanism by increasing its acid phosphatase activity in old shoots for the mobilisation and translocation of P from leaves to roots as a response to soil salinity (López-Berenguer *et al.*, 2007). Development of lateral roots in brassicas (number, length, and growth rate)

can result in higher plant P extraction efficiency traits (Hammond *et al.*, 2009; Akhtar *et al.*, 2008). These better rooting systems increase the effectiveness of accessing sparingly soluble PR through enhanced carboxylic acid extrusion coupled with increased H^+ efflux (Akhtar *et al.*, 2008). The present study is likely to have slightly underestimated the P recovery of both ryegrass and broccoli by disregarding both the root biomass and root P content, especially for broccoli, because of the mechanisms suggested above.

7.4.3 The effect of soil conditions and fertiliser chemical properties on agronomic efficiency

The agronomic performance of DPR-B was higher than other DPR based products with similar or higher citsol P content. This may be partly attributed to the possibility of the biochar content improving the CEC of the subsoil matrix, thereby increasing the potential sink for Ca, Fe, and Al from apatite dissolution via cation exchange. The subsoil had low CEC of 8.7 $cmol_c\ kg^{-1}$ (Table 7.1) which could have limited the sink for apatite dissolution products resulting in a chemical equilibrium that stops the forward reaction. This CEC effect can significantly reduce apatite dissolution as other researchers have noted (Nying and Robinson, 2006). When other P sources are used, such as sintered products, there may be very little effect on the soil CEC compared to when a biochar-based product is used. The sintered P sources (DPRG1, DPR-G2, and DPR-S) have high Ca solubility (42.7 – 45.7 mg citsol Ca/ g) as shown in previous studies, (Chapter 4, section 4.3.6, Tumbure *et al.* (2020b)). The addition of these sintered P sources will potentially increase the soil solution Ca and potentially depress apatite dissolution as the Ca concentration increases if removal from the rhizosphere is less efficient. The efficient removal of dissolution products, such as Ca and P in the rhizosphere, by processes such as plant uptake and cation exchange may increase solubilisation of less reactive P sources (Rafael *et al.*, 2018; Ramirez and Lizaso, 2006).

The poor performance of DPR-S could result from the fact that the serpentine contains 5.18% Fe which could form iron phosphates during sintering (Tumbure *et al.*, 2020b). These iron phosphates may well be more soluble in 2% citric acid than in the plant rhizosphere (Kratz *et al.*, 2019; Vaclavkova *et al.*, 2018). The high concentration of Mg in serpentine are unlikely to have influenced yield since only 0.1% of the Mg in the serpentine rock is water-soluble (Hanly *et al.*, 2005). However, the sintering process employed in the production of the DPR-S fertiliser was shown to result in a citric acid solubility of 7% of the Mg content in the final product (Tumbure *et al.*, 2020b).

The subsoil used in the current experiment had numerous properties that are known to negatively influence dissolution of less reactive P sources. For instance, a pH of 7.2 and a high base saturation of 82%, driven primarily by Mg saturation (41%) (Table 7.1) was measured in the subsoil. However, an advantage of this growing medium was its low available P content (Olsen P 6.3 mg P kg^{-1}), which ensured a growth response to P and therefore capable of testing the agronomic effectiveness of the fertilisers. Compared to observed P uptake in the neutral pH subsoil in this study, improved P uptake is likely to occur in tropical soils with lower pH and lower base saturation, favouring increased PR dissolution rates (Végh *et al.*, 2009; Yusdar *et al.*, 2007).

Of the sintered glass P sources, the DPR-G1 performed agronomically better than DPR-G2, likely because the latter could have led to more Na accumulation in the rhizosphere soil solution. Nakamura *et al.* (2016), when working with Na_2CO_3 sintered PR, reported that Na accumulation in the rhizosphere significantly limited maize growth. Further studies to analyse the exchangeable Fe, Al, Mg, and Na from P sources used in this study is recommended to ascertain the effect of P interaction effects with other elements.

7.4.4 Practical implications and cost issues

A vegetable growing guide by National Tested Seeds Zimbabwe pvt Ltd (N.T.S., 2020) provides a general P fertiliser recommendation of 73 – 92 kg P ha^{-1} when growing broccoli in Zimbabwe. Assuming soil bulk density is 1.0 g cm^{-3}, this translates to approximately 73 – 92 mg P kg^{-1} soil in the topsoil (0- 10 cm). This would require an addition of 287 - 362 kg of MCP (25.4% P) ha^{-1}. Assuming the citsol P in SSP (85% of TP) performs the same as that of MCP, then based on the citsol P substitution rates for broccoli calculated (@ 60 mg citsol P kg^{-1}) in this study (Section 7.3.3; Table 7.4), to supply the same amount of plant available P (92 kg ha^{-1}) would require 1.27 t ha^{-1} SSP, or 2.83 t ha^{-1} DPR-G1, or 3.57 t ha^{-1} DPR, or 3.18 t ha^{-1} DPR-B.

Estimated total cost of materials, transport, and energy, required to manufacture the previously mentioned quantities, will result in a cost of $409, $289, and $553 USD for DPR-G1, DPR-B, and DPR, respectively (Table 7.5). The price of 50 kg of SSP bought in Harare is about $25.50 USD (AMA, 2018), so 1.27 tonne of SSP would cost $670 including the cost to transport it 220 km from Harare to Buhera communal farming area. The cost for road transportation was estimated at US$0.08 $tonne^{-1}$ km^{-1} from a range of between US$ 0.04 – 0.11 $tonne^{-1}$ km^{-1} reported in literature (Vilakazi, 2018; Thando and Anthea, 2017). The unit cost of heating at $0.06 US/kg product was obtained from calculations shown in Appendix 2: Table S7.4. A basic economic analysis reveals that the use of DPR-B or DPR-G1 as P fertilisers can result in a saving of about 57 and 39% (Table 7.5), respectively, compared to using SSP.

Table 7.5 Details for preliminary costing of supplying 92 kg citsol ha^{-1} as various P fertilisers for broccoli cropping

Fertiliser	Total P (%)	Citsol P (%)	Substitution Ratio	Amount of DPR (kg)	Amount of additive (kg)	Cost of materials + transport ($)[a]	Energy cost ($)[b]	Total cost $
MCP	25.4	100	1	-	-	-	-	-
SSP	8.5	85	1	0	0	672	0	672
DPR-G1	8.5	34.2	1.91	1413	1413	240	283	522
DPR-G2	5.6	39.1	0.45	3257	6514	601	977	1578
DPR-B	5.6	33.6	2.74	1055	6329	194	159	352
DPR	16.5	12.1	2.24	3572	0	553	0	553

[a]DPR @ US$0.15 kg^{-1}, SSP @ US$0.51 kg^{-1} (AMA, 2018), glass @ US$0.01 kg^{-1}, transport @US$0.08 $tonne^{-1}$ km^{-1} (Vilakazi, 2018; Thando and Anthea, 2017), [b]Heating energy @ US$0.06 kg^{-1}, SR for 60 mg citsol P kg^{-1} soil.

The cost of a pyrolyser or furnace is not factored in as it can be community-constructed to serve a large group of farmers. Energy costs contribute about 41% and 33% of the total cost of producing DPR-G1 and DPR-B, respectively, and alternative energy sources (for example solar energy) may result in greater savings. Technologies such as solar horizontal bubbling fluidised beds (Baeyens *et al.*, 2019) and solar pyrolysis (Rony *et al.*, 2019) have the potential to further improve sustainability and reduce running costs. Other cost cutting measures such as the use of pyrolysis condensate and gas as energy sources for pyrolysis can be explored (Vitasari *et al.*, 2015).

7.5 Conclusions

Glasshouse trials with ryegrass and broccoli showed that low cost P fertilisers made by either sintering igneous DPR with waste bottle glass (DPR-G1), or pyrolysis of DPR with corn stover (DPR-B) can grow biomass and produce P uptakes either comparable to, or greater than plants fertilised with MCP. Both fertilisers had high substitution rates when applied on a citsol-P basis, and initial costing indicates that they may be a more cost-

effective alternative to commercial SSP in southern Zimbabwe. Improvement of the agronomic value of low solubility PRs through glass sintering or pyrolysis with wastes should be investigated in impoverished regions where manufactured P fertiliser supply is costly and insecure. Repeated field studies with DPR-G1 and DPR-B are recommended with grasses, brassica crops and maize. In addition, field studies should further investigate the ability of brassicas to use DPR as a P source.

Experiments presented in this chapter and the discussion of the results satisfies the thesis objective of evaluating biochar-based, glass-sintered and serpentine sintered P sources involving DPR, on growth and P uptake of annual ryegrass (*Lolium multiflorum* Lam.) and broccoli (*Brassica oleracea* var. italica).

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Chapter 8

OVERALL SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

8.1 Overall summary

The current impact of fertiliser-use on agricultural land quality in the world exists as two contrasting scenarios. In highly industrialised affluent countries, the pollutive effects of excess use of water-soluble P fertilisers are often evident, while in less affluent and less industrialised countries there is soil nutrient mining as a result of the lack of sufficient quantities of external fertiliser inputs. The need for more accurate recommendations for fertiliser use, and methods to produce alternative and less costly P fertilisers are potentially attractive ways to solve these issues. Where external inputs are lacking, there is a requirement for local P resources, aided by improving the P solubility of these poorly soluble P sources. Developing technology may be able to produce controlled-release P fertilisers that may improve P uptake and use efficiency. The development of slow release P fertilisers to achieve low dose synchrony with plant requirements, reduces the incidence of P fixation or losses, and may be able to provide fertilisers at a lower cost, so providing a number of potentially practical solutions.

This thesis focussed on the development and testing of alternative methods to improve the agronomic effectiveness of an igneous phosphate rock (PR) that is locally available in Zimbabwe. In the development of alternative methods, issues associated with costs, practicality, and environmental sustainability, are considered. Characterisation of the current Dorowa PR (DPR) was conducted (achieving the 1st thesis objective), establishing a working research platform by ascertaining the quality of DPR and noting potential problematic contaminant elements that may be transferred to potential final fertiliser products (e.g. fluoride and cadmium content). This thesis then focused on the development of different technologies to improve the reactivity of the DPR and evaluated the resulting P reactivity at laboratory scale (achieving the 2nd, 3rd, and 4th thesis

objectives). Developed technologies, such as sintering with recycled soda glass, co-pyrolysis with maize stover residues, and leaching of DPR to recover P using pyrolysis condensate, were evaluated. Products with observed P reactivity/solubility improvements were assessed in glasshouse trials to test if these observations translated to improved agronomic effectiveness in a soil-plant interface (achieving the 5th thesis objective).

8.1.1 Considerations on the quality of phosphate rock

Characterisation of the DPR that is currently being mined in Zimbabwe indicated that it contains 11% more apatite and about 50% less calcite and other gangue minerals compared to previously reported mineralogical modal concentrations (Chapter 3, published as; Tumbure, A., Bretherton, M. R., Bishop, P. & Hedley, M. J. (2019) Updated Characterization of Dorowa Phosphate Rock Mined in Zimbabwe. Natural Resources Research. 29, 1561–1570 https://doi.org/10.1007/s11053-019-09567-5). The concentrate has a total P content of 16.5% which represents a 2% increase from previously reported values, despite P reactivity remaining constant. Because of the similar mineralogy of the main crystalline components compared to previous reports, it is likely that there have been improvements in the mining and beneficiation process, or the current grade of the ore has a higher apatite content. However, DPR has low potential for use as a direct application phosphate fertiliser without further modification, as confirmed by its low solubility in standard reagents. Because of this low reactivity, direct application of DPR without modification would be agronomically ineffective (Govere *et al.*, 2003), so methods to improve agronomic efficiency are needed. The low levels of total fluoride and cadmium in the DPR indicates that there will be low soil contamination issues associated with fertiliser products developed from DPR.

8.*1.2 Potential of agronomic improvement of igneous phosphate rocks*

This section summarises the results from the various alternative methods proposed in this thesis, and then developed and assessed with the aim of providing increased plant available P from the DPR (Chapter 4-6). Two papers from this work have been published (Chapter 4; Tumbure, A., Bishop, P., Hedley, M. J. & Bretherton, M. R. (2020) Increasing phosphorus solubility by sintering igneous Dorowa phosphate rock with recycled glass. Journal of Thermal Analysis and Calorimetry. https://doi.org/10.1007/s10973-020-10078-2, and Chapter 5; Tumbure, A., Bishop, P, Bretherton, M. and Hedley M. (2020). Co-pyrolysis of maize stover and igneous phosphate rock to produce potential biochar-based phosphate fertilizer with improved carbon retention and liming value. ACS Sustainable Chemistry & Engineering. 8 (10), 4178 - 4184. https://doi.org/10.1021/acssuschemeng.9b06958).

Thermal alteration of the DPR, when combined with various silicate sources and at sub fusion temperatures, was investigated as an alternative method to improve agronomic efficiency (Chapter 4). Mixtures of igneous DPR with recycled glass/dunite/serpentine were heated in a furnace at either 900 or 1000 ^{0}C. After heating, X-ray diffraction analysis revealed that DPR + glass mixtures contained iron silicate ($Fe_2(SiO_4)$), wollastonite ($CaSiO_3$), quartz (SiO_2), and hydroxy-fluorapatite. Resulting increases in citric soluble P were 62, 73, and 44%, compared to the raw DPR when mixed at 1:2, 1:1, and 2:1 (DPR/ glass), respectively. Compared to raw DPR + glass mixtures, corresponding increases in the Ca solubility of heated glass mixtures was in the range of 19 – 35%, confirming the removal of Ca from the apatite structure as a result of Mg^{2+}/Na^{+} substitution. Dissolution results revealed that heated DPR + glass mixtures have potential for use as slow release fertilisers due to increased reactivity. Using recycled glass offers the advantage of reducing manufacturing costs and could be an environmentally friendly option for

disposing of glass. The risk of raising the soil background levels of potentially toxic contaminants such as Sr, Zr, Ba, and Pb, by using recycled glass in this process was found to be insignificant due to the low content of these elements in the glass (at ≤ 90.3 mg kg $^{-1}$). The DPR + glass products were subsequently selected for glasshouse trials (Chapter 7).

Co-pyrolysis of DPR with maize stover was also evaluated as an alternative method to improve the reactivity of the DPR (Chapter 5). Here, DPR was combined with dried and ground maize residues (stems + leaves) at ratios of 1:2, 1:4, 1:6, and 1:8 (w/w), and pyrolysed at 450 ^{o}C for 30 or 60 minutes to produce a suite of biochar-based fertilisers (BBFs). Compared to the unamended DPR, co-pyrolysis resulted in citric soluble P increases of at least 30% for the 1:6 and 1:8 DPR + maize mixes. Observed additional advantages included increases in biochar yields, retained carbon (a small C sink value) and nitrogen, and improved liming value compared to maize stover biochar. While production and soil application of biochar is a viable option when dealing with agricultural residues while improving soil condition, co-pyrolysed biochar could have greater potential to provide plant available P. The DPR + maize stover (1:8) BFF was thus selected for glasshouse trials (Chapter 7)

Pyrolysis condensate is a by-product of the pyrolytic process and is usually disregarded when the focus is on producing biochar for soil application. However, its disposal, or use as fuel, presents challenges due to its high organic acid content. This thesis explored the potential of using aqueous phase pyrolysis liquid as a cheap source of organic acids to solubilise P from DPR (Chapter 6). Firstly, the limits of P recovery from DPR by citric, acetic, and oxalic acids (0.1M) at various pH values were evaluated through single and

sequential titrations. Oxalic acid cumulatively liberated 46% of the total P from DPR after 3 extractions at pH 3, while citric acid cumulatively liberated 22% under the same conditions. However, aqueous phase pyrolysis liquid from maize stover pyrolysis could only recover 14% of the total P in DPR under a pH regime of between 3 to 3.8 in leachates from sequential extractions spaced over 26 hours. The poor solubilisation was probably due to the low concentrations of complexing acids (such as oxalic acid) in the pyrolysis liquid, with the dominant acid being acetic acid at 0.41 moles L^{-1}.

8.1.3 P availability to plants of altered igneous p rock products

Selected alternative P sources that were produced from work conducted in Chapter 4 and 5 were assessed for agronomic effectiveness under ryegrass (*Lolium multiflorum* Lam.) and broccoli (*Brassica oleracea* var. italica) cropping in a glasshouse (Chapter 7). The respective crops were grown in pots fertilised with the alternative P sources and applied at 60 or 120 mg citric acid soluble P kg^{-1} soil. Biochar-based (1:8 DPR/maize stover pre-pyrolysis mix) and glass-sintered fertilisers (with 50% glass) were found to be agronomically effective, producing at least 95% of the ryegrass biomass produced by the mono calcium phosphate (MCP) treatment, and having similar P uptake when applied at 60 mg citric acid soluble P kg^{-1} soil. Similar agronomic effectiveness was observed under broccoli cropping for the same P sources, producing biomass yields and P uptake that was either comparable, or higher, than that of the MCP treatment. Results from this chapter (Chapter 7) confirmed that the observed changes in reactivity at laboratory scale (Chapter 4 and 5) led to an improvement in P bioavailability. However, citric soluble P may not always be a reliable estimator of bioavailable P for all the P sources tested. P sources produced from co-pyrolysis and glass sintering could potentially provide viable P fertiliser options for smallholder farmers around the Dorowa area in Zimbabwe where phosphate rock is mined.

8.1.4 Thesis highlights

- An up to date characterisation of DPR was completed (Chapter 3). Levels of contaminants such as Cd were found to be low, and thus are not of immediate concern.
- Heating DPR with recycled glass at sub fusion temperatures, typically achieved in local brick kilns, was shown to improve the citric acid solubility of P and Ca (Chapter 4). This could provide a practical method for improving the agronomic value of DPR and reduce production costs at site of use.
- Co-pyrolysis of DPR with maize stover could be scaled for local use and was shown to improve C and N retention in biochar. The resultant product had greater citric soluble P than DPR alone (Chapter 5).
- Oxalic acid was found to be highly effective at dissolving P from DPR, while maintaining the lowest concentrations of Ca in solution. Pyrolysis condensate was found to be less effective (Chapter 6).
- While oxalic acid was shown to be effective dissolving P from DPR, the high cost of oxalic acid would make this option prohibitive. Methods for the low-cost production of this acid are essential to pursue this option further (Chapter 6).
- Application of a biochar-based P fertiliser and glass-sintered P fertilisers, was found to be agronomically effective when ryegrass and broccoli were grown in a glasshouse (Chapter 7) and have potential to be economically viable at field scale.

8.2 Recommendations for future research

- **Field testing of developed P fertilisers**

Although selected biochar-based P fertiliser and glass sintered P fertilisers performed well in the glasshouse, there is a need to evaluate their performance at field scale since a

combination of environmental factors and soil type can alter the agronomic effectiveness of fertilisers. Particular attention should focus on evaluating the performance of biochar-based P fertilisers in non-responsive low fertility soils, areas of which are on the increase as a result of nutrient mining in many African smallholder farming regions (Kihara *et al.*, 2016; Mtangadura *et al.*, 2017).

- **Bio-availability analysis of contaminating elements in developed P fertilisers**

The potential risk of raising soil background levels of elements such as Pb and Ba through the use of recycled glass in the sintering process was found to be very low due to their low concentrations. However, a quantitative assessment of the bioavailability of contaminants resulting from the addition of glass-sintered P fertiliser is likely to be needed. An analysis of the speciation of contaminating elements after several applications of the P fertilisers, and an analysis of bioavailability is recommended. Analytical techniques such as X-ray adsorption near-edge structure (XANES) spectroscopy would prove to be essential in speciation analysis.

- **Alternative methods for producing chelating and complexing organic acids, and varying leaching conditions**

Research into how pyrolysis reaction conditions can be altered to favour production of higher acid titers of oxalic and citric acids used for igneous PR dissolution is recommended. Fermentation may offer an alternative method to produce organic acids for PR dissolution and should be explored. Further kinetic investigations to improve P dissolution by using a flooded pyrolysis liquid recycling system is also warranted to quantify the effect of contact time.

- **Economical methods to achieve sintering temperatures using green energy.**

Research to further reduce costs of sintering or fusion using solar kilns is recommended. Technologies such as a solar horizontal bubbling fluidised bed are currently being developed (Baeyens *et al.*, 2019) and will need to be adapted to emerging PR amelioration techniques. One of the biggest challenges of flameless calcination using solar power is the high cost of the equipment (Haneklaus *et al.*, 2017). Further development of this technology would allow the harnessing of concentrated solar power so that PR fusion processes are more economical. In both pyrolysis and sintering, a low-cost solar furnace could be used to dry feedstocks and to raise the initial pyrolysis/sintering temperatures.

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APPENDIX

Appendix 1. Supporting information for Chapter 4 (S4)

Table S4.1 Selected citric acid soluble elements from raw (un-sintered) mixtures

Mixture	Initial DPR content (%)	Citric acid soluble (mg g^{-1})				
		Ca	Mg	Na	Fe	Al
DPR: Soda Glass	33	31.6 ± 0.4	0.3 ± 0.003	2.8 ± 0.02	0.3 ± 0.01	0.2 ± 0.01
DPR: Soda Glass	50	38.2 ± 0.2	0.3 ± 0.004	2.3 ± 0.02	0.4 ± 0.003	0.3 ± 0.01
DPR: Serpentine	33	29.0 ± 0.3	8.3 ± 0.1	0.6 ± 0.003	1.3 ± 0.01	0.8 ± 0.01
DPR: Serpentine	50	35.6 ± 0.2	6.3 ± 0.1	0.6 ± 0.01	1.1 ± 0.02	0.7 ± 0.03
DPR: Dunite	33	28.8 ± 0.1	4.5 ± 0.01	0.6 ± 0.01	3.1 ± 0.04	1.0 ± 0.01
DPR: Dunite	50	34.9 ± 0.1	3.7 ± 0.03	0.6 ± 0.01	2.5 ± 0.02	0.9 ± 0.01
DPR	100	49.7 ± 0.1	0.3 ± 0.01	0.7 ± 0.04	0.7 ± 0.01	0.5 ± 0.04
Soda Glass	-	2.0 ± 0.03	0.4 ± 0.01	5.1 ± 0.5	0.1 ± 0.00	0
Serpentine	-	1.0 ± 0.1	15.4 ± 0.2	0.1 ± 0.02	1.3 ± 0.03	0.4 ± 0.01
Dunite	-	2.0 ± 0.03	7.7 ± 0.1	0.4 ± 0.002	4.1 ± 0.1	0.6 ± 0.003

numbers after ± are standard errors of means (n=3)

Table S4.2 Selected citric acid soluble elements vs soluble P molar ratios

Mixture	Initial DPR content (%)	Ca:P molar ratio	Mg:P molar ratio	Na:P molar ratio	Fe:P molar ratio	Al:P molar ratio
Sintered at 1173 K						
DPR: Soda Glass	33	1.51	0.02	0.40	0.01	0.01
DPR: Soda Glass	50	1.21	0.01	0.23	0.002	0.01
DPR: Serpentine	33	1.33	0.60	0.05	0.03	0.02
DPR: Serpentine	50	1.59	0.47	0.04	0.02	0.03
DPR: Dunite	33	1.56	0.60	0.07	0.04	0.04
DPR: Dunite	50	1.66	0.46	0.05	0.03	0.05
Raw mixtures (not heated)						
DPR: Soda Glass	33	1.83	0.02	0.29	0.005	0.01
DPR: Soda Glass	50	1.83	0.02	0.19	0.004	0.02
DPR: Serpentine	33	1.68	0.80	0.06	0.02	0.06
DPR: Serpentine	50	1.70	0.49	0.05	0.01	0.05
DPR: Dunite	33	1.67	0.43	0.06	0.05	0.09
DPR: Dunite	50	1.67	0.29	0.05	0.03	0.06
DPR	100	1.92	0.02	0.04	0.004	0.03
Extra solubilised elements (sintered – raw mixtures)						
DPR: Soda Glass	33	1.01	0.01	0.56	0.001	0.01
DPR: Soda Glass	50	0.45	0.00	0.28	-0.002	-0.005
DPR: Serpentine	33	0.93	0.36	0.03	0.01	-0.02
DPR: Serpentine	50	1.42	0.44	0.01	0.01	-0.004
DPR: Dunite	33	1.35	0.91	0.08	-0.01	-0.04
DPR: Dunite	50	1.66	0.81	0.03	-0.003	0.04

Appendix 2. Supporting information for Chapter 7 (S7)

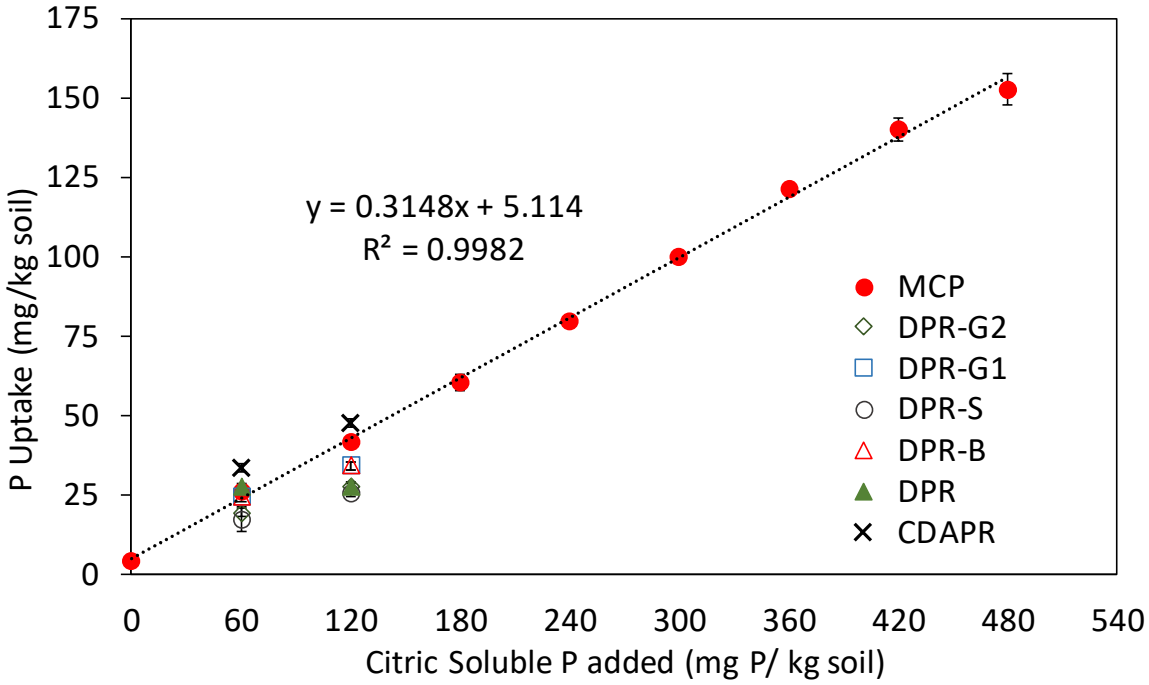

Figure S7.1 Relationship between ryegrass cumulative P uptake (after 6 harvests) and citsol P applied. Error bars represent 2x SEM (n = 4)

Table S7.1 P concentration in ryegrass shoots at each harvest

	% P in shoots at 60 mg P / k g						% P in shoots at 120 mg P / kg					
Harvest	**1**	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**	**5**	**6**
DPR-G2	0.09	0.10	0.11	0.10	0.11	0.15	0.16	0.13	0.11	0.10	0.11	0.14
DPR-G1	0.12	0.11	0.11	0.10	0.11	0.14	0.22	0.15	0.13	0.11	0.11	0.14
DPR-S	0.07	0.12	0.12	0.10	0.11	0.13	0.08	0.15	0.13	0.10	0.11	0.15
DPR	0.07	0.15	0.13	0.11	0.12	0.14	0.06	0.16	0.13	0.10	0.11	0.14
CDAPR	0.13	0.13	0.13	0.11	0.14	0.18	0.16	0.17	0.17	0.15	0.18	0.21
MCP	0.16	0.11	0.10	0.11	0.13	0.16	0.15	0.11	0.10	0.15	0.23	0.30
DPR-B	0.08	0.14	0.13	0.11	0.11	0.14	0.15	0.14	0.13	0.12	0.13	0.17
No P	0.08	0.08	0.09	0.09	0.10	0.10	-	-	-	-	-	-

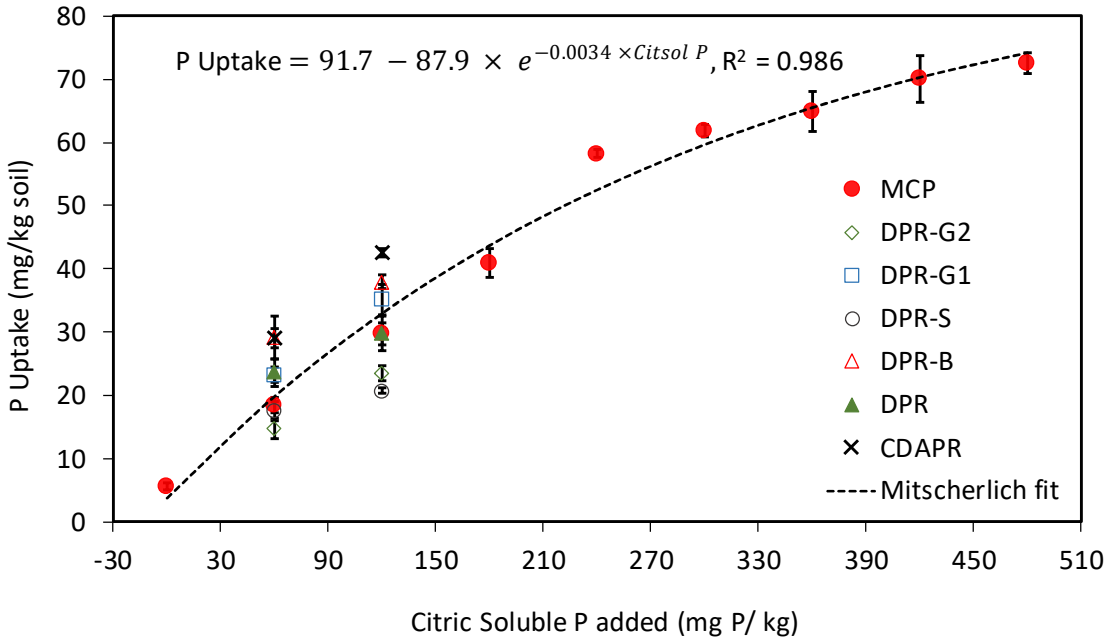

Figure S7.2 Relationship between broccoli P uptake and citric soluble P applied at 68 days after transplanting. Error bars represent 2x SEM (n = 4)

Table S7.2 P concentration in broccoli biomass harvested at 68 days after transplanting

P source	% P in shoots at 60 mg P / k g	% P in shoots at 120 mg P / k g
DPR-G2	0.10 ± 0.008	0.10 ± 0.004
DPR-G1	0.11 ± 0.006	0.14 ± 0.011
DPR-S	0.09 ± 0.008	0.11 ± 0.001
DPR	0.11 ± 0.015	0.15 ± 0.021
CDAPR	0.15 ± 0.017	0.19 ± 0.012
MCP	0.09 ± 0.012	0.14 ± 0.012
DPR-B	0.12 ± 0.011	0.18 ± 0.008
No P	0.05 ± 0.003	-

Numbers after ± are standard errors of means (SEM)

Table S7.3 Physiological efficiency of broccoli and ryegrass

P rate	**60 mg P/kg**						**120 mg P/kg**						
P Source	**DPR-G2**	**DPR-G1**	**DPR-S**	**DPR**	**CDA-PR**	**MCP**	**DPR-B**	**DPR-G2**	**DPR-G1**	**DPR-S**	**DPR**	**CDA-PR**	**MCP**	**DPR-B**
Broccoli														
	0.65	0.60	0.97	0.62	0.46	0.78	0.50	0.70	0.41	0.58	0.51	0.35	0.51	0.36
Cumulative Ryegrass harvests														
1st harvest	0.93	0.69	2.17	7.07	0.66	0.53	1.17	0.45	0.37	1.16	< 0	0.49	0.28	0.56
2nd harvest	0.93	0.80	0.74	0.55	0.72	0.63	0.71	0.61	0.51	0.61	0.52	0.53	0.34	0.63
3rd harvest	0.91	0.82	0.71	0.62	0.73	0.72	0.73	0.71	0.60	0.68	0.62	0.54	0.43	0.67
4th harvest	0.92	0.87	0.77	0.69	0.76	0.78	0.78	0.79	0.67	0.75	0.73	0.56	0.52	0.71
5th harvest	0.91	0.88	0.78	0.71	0.75	0.80	0.80	0.81	0.71	0.77	0.76	0.55	0.55	0.72
6th harvest	0.87	0.84	0.75	0.69	0.71	0.77	0.78	0.80	0.70	0.75	0.74	0.54	0.56	0.69

Costing details and calculations

Table S7.4 Power cost

Option 1 Electric furnace	**Option 2** Coal powered brick kiln
Energy requirement for sintering between 850 -1000 ºC is about 800kcal/kg or 3.35MJ/kg (Abouzeid, 2008) This translates to 0.931 kWhr/kg of product Electricity costs $4.88 ZWL /kWhr (Muhamba, 2020) This translates to $0.058 US/kWhr using the current average USD auction rate of $85 ZWL: $1 USD (Vinga, 2020) Power cost for sintering then comes to: 0.931 kWhr/kg x $0.058 US/kWhr = **$0.054 US/kg**	Energy requirement for sintering at around 900 ºC is about 2.5 MJ/kg (Prasertsan *et al.*, 1997) Local coal from Zimbabwe has a calorific value of 25.45 MJ/kg (Maqhuzu *et al.*, 2020), therefore 0.098 kg of coal would be required per kg of product Cost of purchasing coal at source is $0.065 US/kg of coal (Maqhuzu *et al.*, 2020) Cost of transporting the coal would be 655 km (distance from Hwange to Buhera) x $0.00008US /kg/km (Vilakazi, 2018; Thando and Anthea, 2017) = $0.0524 US/kg Power cost for sintering then comes to: $0.065 US/kg x 0.098 (coal) + $0.0524 US/kg (transport) = **$0.059 US/kg**

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Appendix 3. Statement of Contribution forms (DRC-16)

DRC 16

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STATEMENT OF CONTRIBUTION
DOCTORATE WITH PUBLICATIONS/MANUSCRIPTS

We, the candidate and the candidate's Primary Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated below in the *Statement of Originality*.

Name of candidate:	Akinson Tumbure
Name/title of Primary Supervisor:	Michael J. Hedley/ Emeritus Professor
In which chapter is the manuscript /published work:	Chapter 3

Please select one of the following three options:

(●) The manuscript/published work is published or in press

- Please provide the full reference of the Research Output:

Tumbure, A., Bretherton, M. R., Bishop, P. & Hedley, M. J. (2019). Updated Characterization of Dorowa Phosphate Rock Mined in Zimbabwe. Natural Resources Research. 29, 1561–1570. https://doi.org/10.1007/s11053-019-09567-5

( ) The manuscript is currently under review for publication – please indicate:

- The name of the journal:

- The percentage of the manuscript/published work that was contributed by the candidate: 95.00

- Describe the contribution that the candidate has made to the manuscript/published work:

Idea conception,
Laboratory analysis,
Data entry, collation and analysis,
Manuscript writeup, submission, corresponding author and editing

( ) It is intended that the manuscript will be published, but it has not yet been submitted to a journal

Candidate's Signature:	Akinson Tumbure Digitally signed by Akinson Tumbure Date: 2020.10.19 11:43:38 +13'00'
Date:	19-Oct-2020
Primary Supervisor's Signature:	M.J.Hedley Digitally signed by M.J.Hedley Date: 2020.10.19 12:02:56 +13'00'
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This form should appear at the end of each thesis chapter/section/appendix submitted as a manuscript/ publication or collected as an appendix at the end of the thesis.

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DRC 16

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Name/title of Primary Supervisor:	Michael J. Hedley/ Emeritus Professor
In which chapter is the manuscript /published work:	Chapter 4

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Tumbure, A., Bishop, P., Hedley, M. J. & Bretherton, M. R. (2020) Increasing phosphorus solubility by sintering igneous Dorowa phosphate rock with recycled glass. Journal of Thermal Analysis and Calorimetry. https://doi.org/10.1007/s10973-020-10078-2

( ) The manuscript is currently under review for publication – please indicate:

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Running experiments
Laboratory analysis,
Data entry, collation and analysis,
Manuscript writeup,submission, corresponding author and editing

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Tumbure, A., Bishop, P, Bretherton, M. and Hedley M. (2020). Co-pyrolysis of maize stover and igneous phosphate rock to produce potential biochar-based phosphate fertilizer with improved carbon retention and liming value. ACS Sustainable Chemistry & Engineering. 8 (10), 4178 - 4184. https://doi.org/10.1021/acssuschemeng.9b06958

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